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Investigation of the Thermal Destructibility of Hazardous Wastes Using the Thermal Decomposition Analytical System

Dayton Univ., OH

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INVESTIGATION OF THE THERMAL DESTRUCTIBILITY OF HAZARDOUS WASTES USING THE THERMAL DECOMPOSITION ANALYTICAL SYSTEM

by

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The laboratory determined gas-phase thermal decomposition characteristics of a variety of hazardous organic compounds and mixtures of organic compounds are reported. The thermal stabilities of the compounds are assessed and compared, and the effects on thermal stability from the variation of several parameters are demonstrated.

Possible chemical mechanisms for the decomposition of the gas-phase species are reported, including mechanisms for the formation of stable products. The role of oxygen in the thermal destruction of chlorinated aromatics is addresssed qualitatively, through proposed reaction mechanisms, and quantitatively, through the application of kinetic methods. The thermal decomposition analytical system used for generation of these data is discussed in limited detail, and modifications performed to improve its utility and sensitivity are discussed.

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FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of solid and hazardous wastes. These materials, if improperly dealt with, can threaten both public health and the environment. Abandoned waste sites and accidental releases of toxic and hazardous substances to the environment also have important environmental and public health implications. The Hazardous Waste Engineering Research Laboratory assists in providing an authoritative and defensible engineering basis for assessing and solving these problems. Its products support the policies, programs, and regulations of the Environmental Protection Agency, the permitting and other responsibilities of State and local governments and the needs of both large and small businesses in handling their wastes responsibly and economically.

This report describes the results of gas phase thermal decomposition studies for hazardous organic compounds and mixtures of organic compounds. These data are important in the overall evaluation of the effectiveness of thermal destruction for control of hazardous waste. For further information, please contact the Alternative Technologies Division of the Hazardous Waste Engineering Research Laboratory.

David G. Stephan, Director
Hazardous Waste Engineering Research Laboratory

ABSTRACT

The laboratory determined gas-phase thermal decomposition characteristics of a variety of hazardous organic compounds and mixtures of organic compounds are reported. The thermal stabilities of the compounds are assessed and compared, and the effects on thermal stability from the variation of several parameters are demonstrated.

Possible chemical mechanisms for the decomposition of the gas-phase species are reported, including mechanisms for the formation of stable products. The role of oxygen in the thermal destruction of chlorinated aromatics is addressed qualitatively, through proposed reaction mechanisms, and quantitatively, through the application of kinetic methods. The thermal decomposition analytical system used for generation of these data is discussed in limited detail, and modifications performed to improve its utility and sensitively are discussed.

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ABBREVIATIONS AND SYMBOLS

A - Arrhenius coefficinet
a - Stoichiometric reaction coefficient, or reaction order
abs - Absolute
amu - Atomic mass unit
atm - Atmosphere
attn - Attenuation
Br - Bromine atom
°C - Degrees centigrade
CFR - Code of Federal Regulations
Cl - Clorine atom
cm - Centimeter
CO_2 - Carbon dioxide
DBB - Dibromobiphenyl
DCB - Dichlorobiphenyl
DDD - 2,2-Bis (chlorophenyl)-1,1-dichloroethane
DDE - 2,2-Bis (chlorophenyl)-1,1-dichloroethylene
DDT - Dichlorodiphenyltrichloroethane
DE - Destruction efficiency
DRE - Destruction and removal efficiency
E_a - Activation energy (kcal/mole^{-1})
eV - Electron volt
f_r - Fraction remaining
GC - Gas chromatography
GC-MS - Gas chromatograph-mass spectrometer
H - Hydrogen atom
H_2O - Water
HCBz - Hexachlorobenzene
HCCPD - Hexachlorocyclopentadiene
HCl - Hydrochloric acid
HRGC - High resolution gas chromatography
ID - Inside diameter
°K - Degrees Kelvin
k' - Pseudo - first order rate constant (s^{-1})
kcal - Kilocalorie
kV - Kilovolt
ln - Natural Logarithm
log - Logarithm
m - Meter
MID - Multiple ion detection
mm - Millimeter
MS - Mass Spectrometry
ms - Millisecond
mV - Millivolt
µA - Microamp
µg - Microgram
µl - Microliter
µm - Micrometer
N_2 - Nitrogen molecule

ABBREVIATIONS AND SYMBOLS CON'T

O - Oxygen atom
O_2 - Oxygen molecule
OCCP - Octachlorocyclopentene
PCB - Pentachlorobiphenyl
PCBz - Pentachlorobenzene
PCN - Polychlorinated naphthalene
PCNB - Pentachloronitrobenzene
PIC - Product of incomplete combustion
POHC - Principal organic hazardous constituent
ppm - Parts per million
R - Universal gas constant (1.99 cal $mole^{-1}$ $°K^{-1}$)
r^2 - Linear coefficient of correlation
s.s. - Stainless steel
T - Temperature
T_{DE} - Temperature required for a given destruction efficiency
T_{99} - Temperature required for 99% destruction efficiency
$T_{99.99}$ - Temperature required for 99.99% destruction efficiency
$\bar{t}_r$ - Mean gas phase residence time(s)
TCBz - Tetrachlorobenzene
TDAS - Thermal decomposition analytical system
TIC - Total ion concentration
UDRI - University of Dayton Research Institute
wt% - Weight percent

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SECTION 1

INTRODUCTION

Based on a recent report [1] from the United States Environmental Protection Agency (US-EPA), 150 million metric tons of federally regulated hazardous waste were generated in the United States during 1981. This new estimate is approximately 100 million tons greater than previous estimates and indicates the magnitude of the problem to be solved by proper treatment methods for detoxification and disposal of hazardous wastes.

Prior to 1976, land disposal, including impoundments, pits, lagoons, and deep wells, received as much as 80 percent of the hazardous waste generated [2]. Then in 1976, Public Law 94-580, the Resource Conservation and Recovery Act was enacted. Included in this act, a Congressional Finding states:

> "disposal of solid waste and hazardous wastes in or on the land without careful planning and management can present a danger to human health and environment."

Under the authority of this law, regulations were subsequently promulgated which require monitoring the integrity of a landfill for a 30-year period. Should leaking of hazardous materials from the landfill occur during this period, the liability for clean-up is placed on the generator of the material. This additional responsibility for the generator has resulted in an increased interest in other methods of hazardous waste disposal.

Incineration, although more immediately costly than landfilling, is seen as an attractive method for the permanent disposal of hazardous organic wastes[3]. In addition, in many instances, organic wastes with sufficient heating value and appropriate physical characteristics are being utilized as supplemental fuels in industrial boilers[4]. Both of these disposal methods involve the virtual destruction of the waste and are therefore considered perferable to containment methods such as landfilling.

Also in 1976, the science of environmentally safe thermal destruction of hazardous organics made significant gains. As a result of pesticide contamination in the James River near Hopewell, Virginia, the US-EPA requested that the University of Dayton investigate the thermal disposal of the offending insecticide Kepone®. Utilizing thermal instrumentation systems designed and developed at the University[5], investigators determined the conditions required for the gas-phase thermal destruction of the insecticide. These parameters provided guidelines for subsequent incineration test burns and the successful destruction of Kepone.

As a result of this study and other laboratory investigations by researchers at the University, two major observations were reported.

1. Most hazardous organic compounds are amenable to thermal destruction.
2. Under certain conditions, hazardous thermal reaction products may form which are more difficult to destroy and may be more toxic than the parent material.

In addition, several variables were identified which play an important role in the gas-phase destruction of the target compound. Three of these variables are:

- exposure temperature,
- mean residence time, and
- composition of reaction atmosphere.

To understand the correlation between gas-phase thermal decomposition results and the complex array of events which occur during incineration, one need only review the various processes in a typical incineration system.

Figure 1.1 is a simplified diagram of an incinerator consisting of rotary kiln and secondary combustion chamber. The destruction zones within this unit have been divided into four categories.

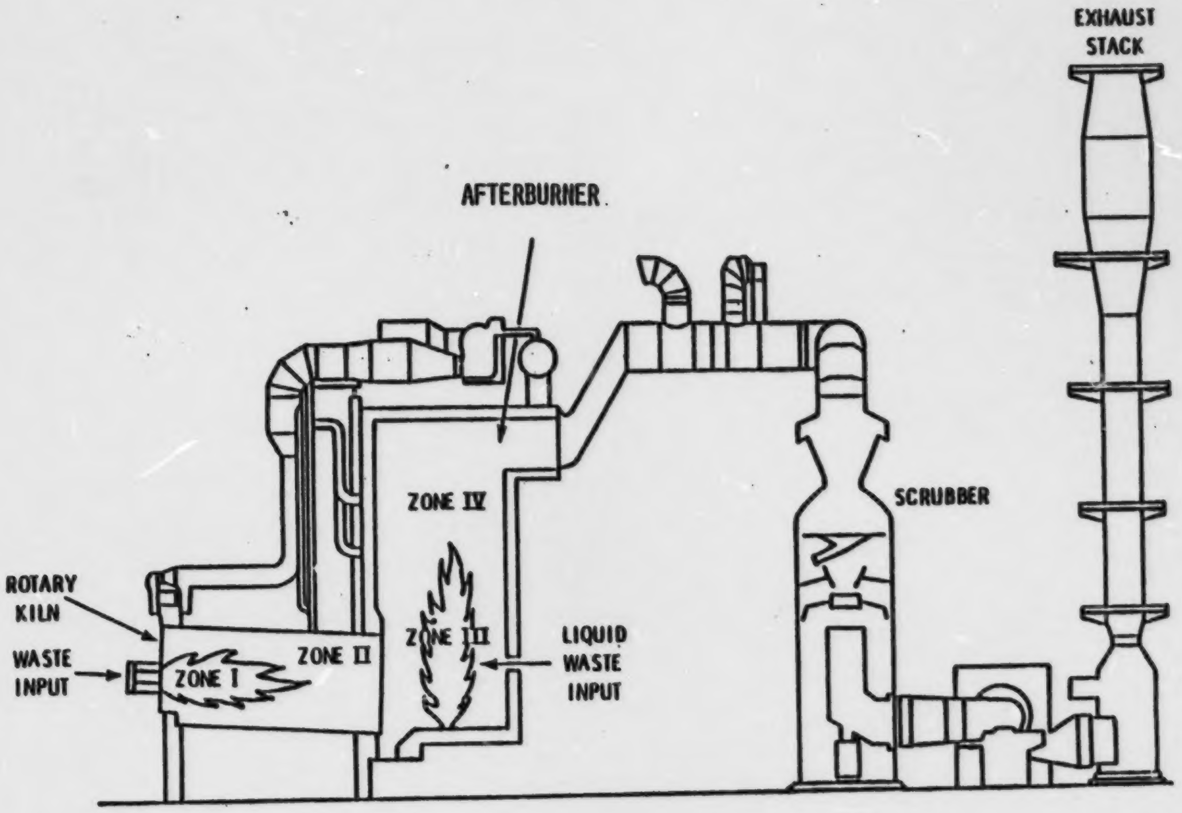

EXHAUST STACK
AFTERBURNER
SCRUBBER
ZONE IV
ROTARY KILN
WASTE INPUT
ZONE I
ZONE II
ZONE III
LIQUID WASTE INPUT

Figure 1.1. Simplified Diagram of an Incineration System Consisting of a Rotary Kiln and Secondary Combustion Chamber. The Four Destruction Zones Discussed in the Text are Labeled in the Figure.

I Rotary Kiln Flame Zone

II Rotary Kiln Thermal Decomposition Zones

III Afterburner Flame Zone

IV Thermal Oxidation Zone

Wastes enter the rotary kiln flame zone and thermal decomposition (non-flame) zones and are gasified by a variety of processes (e.g., sublimation, melting and vaporization, or degradation) depending on the physical state and chemical characteristics of the waste. The vaporized waste may enter the flame resulting in its decomposition. It may interact with reactive species in the kiln's non-flame thermal decomposition zone, or the waste may be vaporized and transported, chemically unchanged, into the afterburner zones. The reactions that occur in the kiln's non-flame and flame zones will result in combustion of the waste materials if conditions are such that ample interaction with reactive oxidizing agents such as O and OH species occur. If conditions are less than ideal and combustion of the waste material is incomplete, reactions occurring in the kiln non-flame zone may generate molecules which have greater thermal stability than those originally present. These molecules along with the molecules that escapt any decomposition in the rotary kiln zones will subsequently enter the afterburner zones.

Except when direct liquid injection is occurring, molecules entering the afterburner zones are primarily already in the gas phase. As in the kiln, a variety of chemical processes occur in and around the afterburner flame. These include both oxidation, leading to complete or incomplete combustion and thermal reactions such as radical recombinations which may form thermally stable products. In any case, these molecules as well as those molecules which by-pass the reactive flame environment pass through the last high-temperature zone, the thermal oxidation (non-flame) zone of the afterburner.

Incompletely oxidized gas-phase material entering the non-flame afterburner zone is subjected to thermal conditions which are characteristic of the design and operation of the particular incinerator. The material that leaves this zone may be in the form of fully oxidized combustion products, products of incomplete combustion, or molecules which have remained intact throughout all four zones. This depends on the reaction atmosphere and duration of exposure in the non-flame afterburner zone as well as the inherent thermal stability of the material entering the zone. This zone is, therefore, the final determinant of the quantity and composition of incompletely combusted material which survives the high-temperature zones of an incinerator. On this basis, one can clearly see the usefulness of non-flame gas-phase studies for ascertaining the incinerability of hazardous organic compounds.

This report presents data and discussions on the non-flame gas-phase thermal decomposition of hazardous organic compounds. Information pertaining to the factors affecting gas-phase thermal decomposition along with associated phenomena are included. Certain aspects of the experimental procedures and instrumentation are discussed in Section 4. Section 5 includes the results and discussions of experiments conducted to elucidate gas-phase thermal stabilities, factors affecting those stabilities, and the formation of products of incomplete combustion. In Section 6, pseudo first-order kinetic methods are used to assess the rates and mechanisms involved in the thermal decomposition of some chlorinated aromatics. Modifications of the thermal decomposition analytical system are addressed in Section 7, and Section 8 is a summary which discusses certain aspects of this work in relation to full-scale incineration. Finally, an appendix describes several examples of direct correlation between laboratory generated gas-phase thermal decomposition data and field studies.

SECTION 2

CONCLUSIONS

- The laboratory approach, using thermal instrumentation systems, has a demonstrated ability to investigate the gas-phase thermal decomposition behavior of organic substances.

  Information obtained from such investigations is useful to insure the safe and economical operation of incinerator systems and can provide guidance for the regulation of such systems.

- Products of incomplete combustion (PICs) are frequently observed when mixtures of hazardous organic compounds and pure compounds are exposed to conditions insufficient for complete oxidation to occur.

- Somewhat limited data indicates that the formation of PICs during the thermal exposure of a mixture may depend more on the propensity of the individual constituents to form PICs than the overall chemistry of the mixture.

- PICs form readily from chlorinated compounds considered thermally stable (e.g., the temperature required for 99.99 percent destruction ($T_{99.99}$) of the compound is greater than 800°C) as well as those of lesser thermal stability (e.g., $T_{99.99} < 650°C$).

- Simple, single carbon chlorinated compounds may serve as precursors for hazardous, structurally complex PICs.

- The oxygen dependence of the thermal decomposition of chlorinated aromatic compounds is important and very complex. It is a function of both the exposure temperature and the degree of chlorination of the compound of interest.

- The relative thermal stabilities of organic compounds as well as the mechanisms of product formation can be explained using the fundamentals of organic chemistry. As the data base for this type of information expands, a priori prediction of the thermal stability of a wide range of compounds should become possible.

- Both complex mixtures of hazardous organic compounds and pure organic compounds can be efficiently destroyed by combustion in the gas phase.

SECTION 3

RECOMMENDATIONS

- Based on the data obtained in this project, alternative permitting processes should be considered to ensure environmentally safe incineration (i.e., destruction of both POHCs and PICs) rather than permitting processes which simply evaluate the destruction and removal of POHCs. For example, the selection of a POHC for trial burn monitoring could be based on gas-phase thermal stability [as measured by the laboratory determined temperature required for 99 or 99.99 percent destruction (T_{99} or $T_{99.99}$)], toxicity, and concentration in the waste. A PIC for emissions monitoring should be selected from a laboratory generated data base identifying the PICs formed from a variety of waste streams. The permit writer should have the option of ordering laboratory testing of unusual waste streams to establish the identity of suitable compounds for monitoring.

  In some cases, a single test compound will fulfill the requirement for both PIC and POHC monitoring. For instance, based on the current data base, hexachlorobenzene would be a suitable compound for assessing the overall combustion efficiency of a waste stream containing chlorinated organics.

- Experimental data indicates that even the simplest chlorinated hydrocarbons may serve as precursors to larger and potentially toxic PICs. Because of this, an intensive research effort should be undertaken to identify the fundamental reactions involved in such pathways.

- If suitable methods cannot be established for preventing PIC formation, the possibility of reducing the overall toxicity of the PICs formed should be investigated. This might involve the addition of chlorine radical scavengers to alter the incineration atmosphere, preventing the formation of toxic chlorinated PICs.

- Laboratory studies should be undertaken to assess the effects of various incinerator failure modes (e.g., reduced oxygen, short residence time, or low temperature) on both POHC destruction and PIC formation. These failure modes should be ranked based on their effect on incineration efficiency.

SECTION 4

EXPERIMENTAL

All of the data presented in this report were generated on the thermal decomposition analytical system (TDAS). This system was designed and built with funding provided by the US-EPA (Grant No. R805117-01-0). A description of the system as well as general and specific experimental details follow.

4.1 INSTRUMENTATION

The TDAS, shown by artist's rendering in Figure 4.1 and in block diagram form in Figure 4.2, is a closed continuous analytical system which allows controlled thermal exposure of gas-phase molecules followed by separation, detection, and identification of the resulting thermal reaction products.

Samples are inserted into the TDAS via a thermally programmable insertion chamber. A variety of probes and insertion methods may be used depending on the physical state of the sample of interest. The two probes used for samples addressed in this report are shown in Figure 4.3. The sand blasted probe was utilized for low volatility solids while the quartz wool packed probe (providing greater surface area) was utilized for liquids and the more volatile solids.

Following vaporization from the probe and into a flowing reaction gas stream, a controlled thermal exposure of the sample occurs in a narrow bore quartz tubular reactor located within a three-zone Lindberg furnace. The reactor assembly is shown in Figure 4.4. The reactor itself is one millimeter inside diameter quartz tubing, one meter in length, folded to enable containment of its entire length within the most thermally uniform central region of the furnace. The sample is carried to and from the reactor in quartz transfer lines maintained at non-degradative transport temperatures through the use of heated conduit and/or heat exchange air

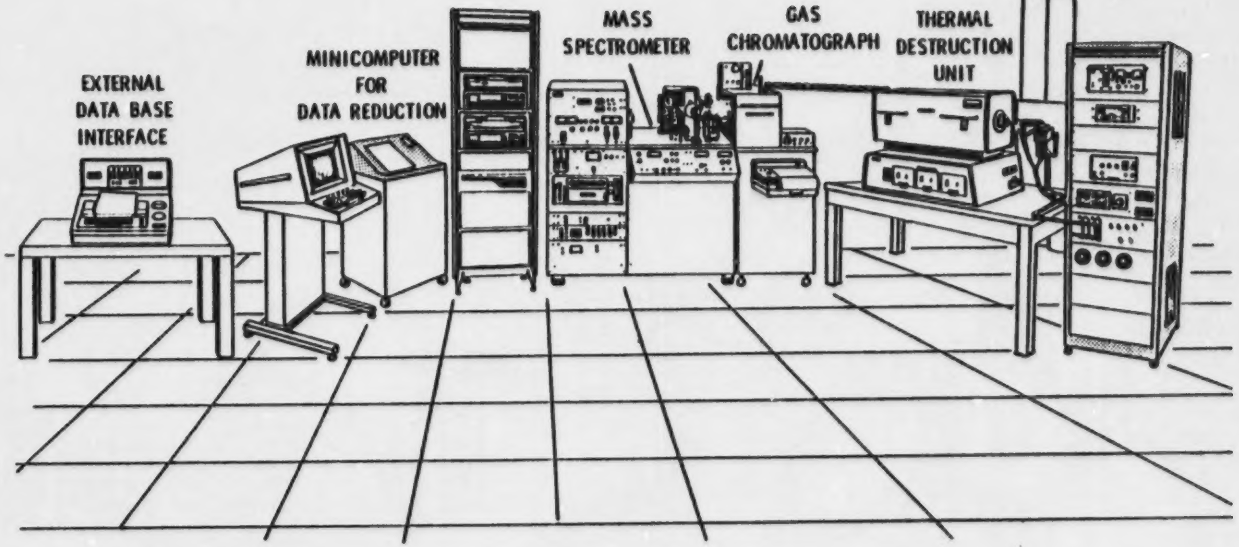
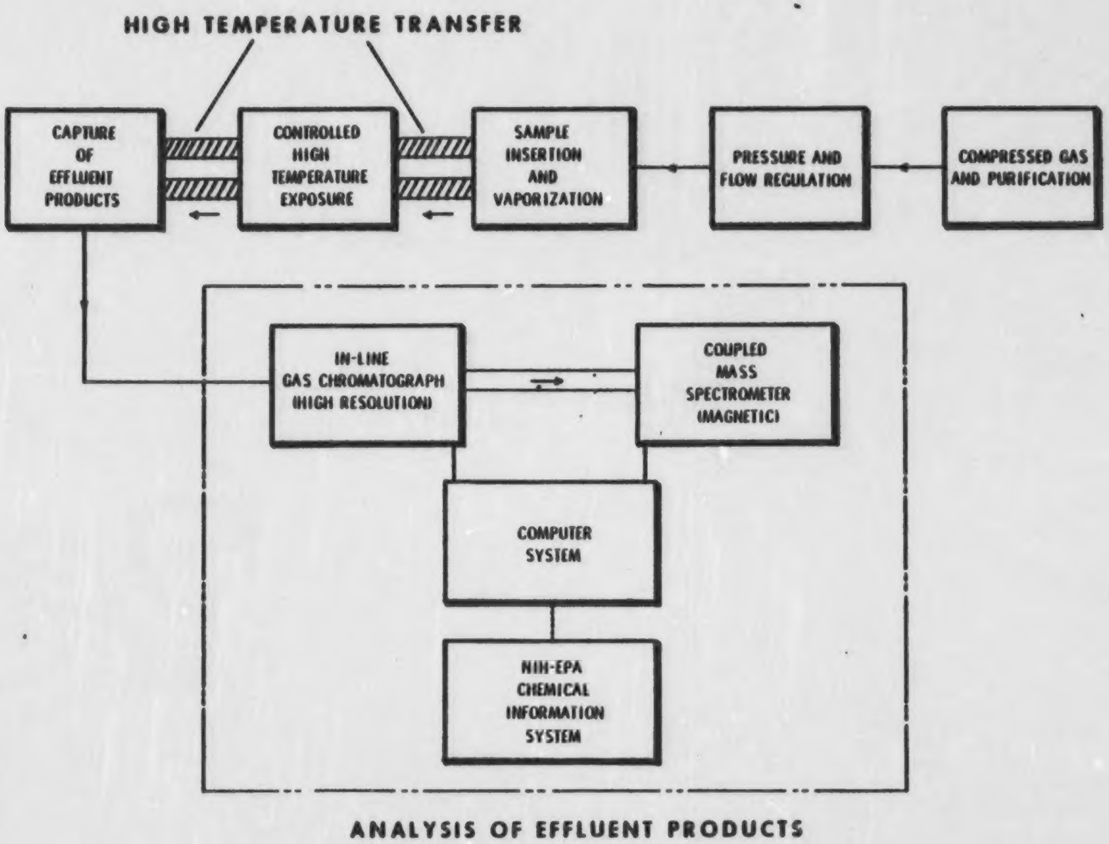

EXTERNAL
DATA BASE
INTERFACE
MINICOMPUTER
FOR
DATA REDUCTION
MASS
SPECTROMETER
GAS
CHROMATOGRAPH
THERMAL
DESTRUCTION
UNIT

Figure 4.1. Artist's Rendering of Assembled TDAS.


HIGH TEMPERATURE TRANSFER
CAPTURE OF EFFLUENT PRODUCTS
CONTROLLED HIGH TEMPERATURE EXPOSURE
SAMPLE INSERTION AND VAPORIZATION
PRESSURE AND FLOW REGULATION
COMPRESSED GAS AND PURIFICATION
IN-LINE GAS CHROMATOGRAPH (HIGH RESOLUTION)
COUPLED MASS SPECTROMETER (MAGNETIC)
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ANALYSIS OF EFFLUENT PRODUCTS

Figure 4.2. Block Diagram of TDAS.

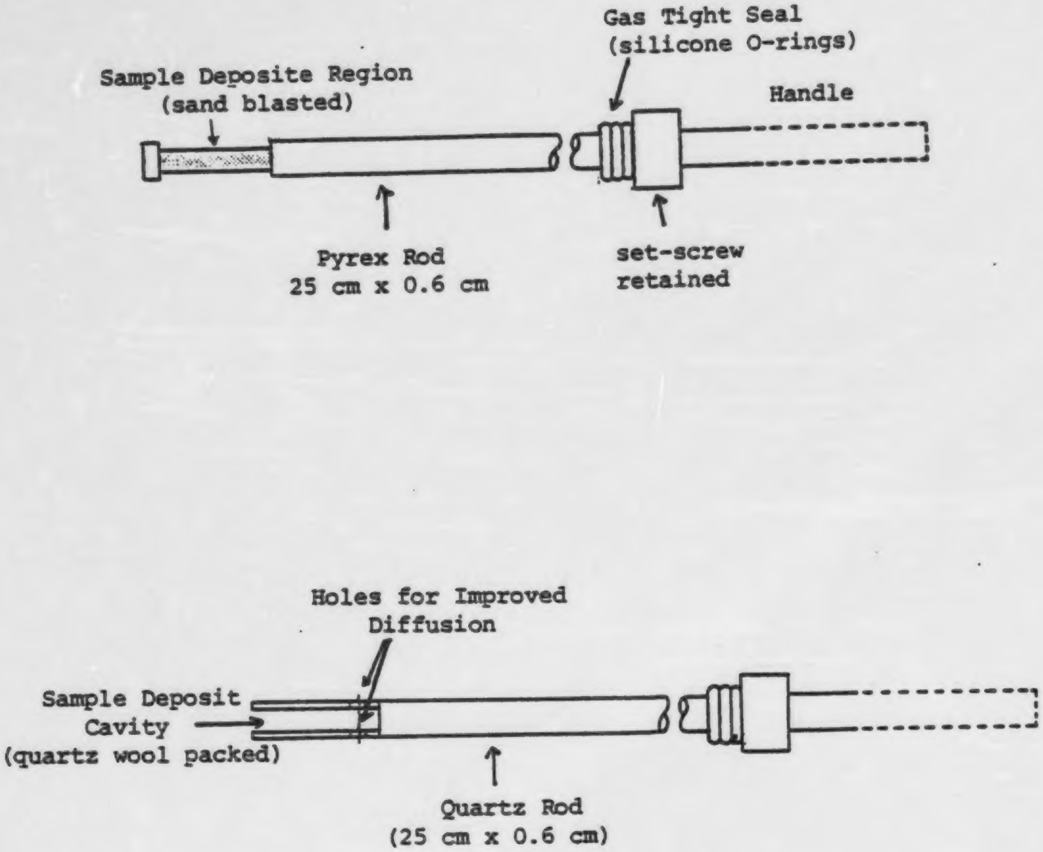

Gas Tight Seal
(silicone O-rings)
Sample Deposite Region
(sand blasted)
Handle
Pyrex Rod
25 cm x 0.6 cm
set-screw
retained
Holes for Improved
Diffusion
Sample Deposit
Cavity
(quartz wool packed)
Quartz Rod
(25 cm x 0.6 cm)

Figure 4.3. Sample Insertion Probes Utilized with TDAS.

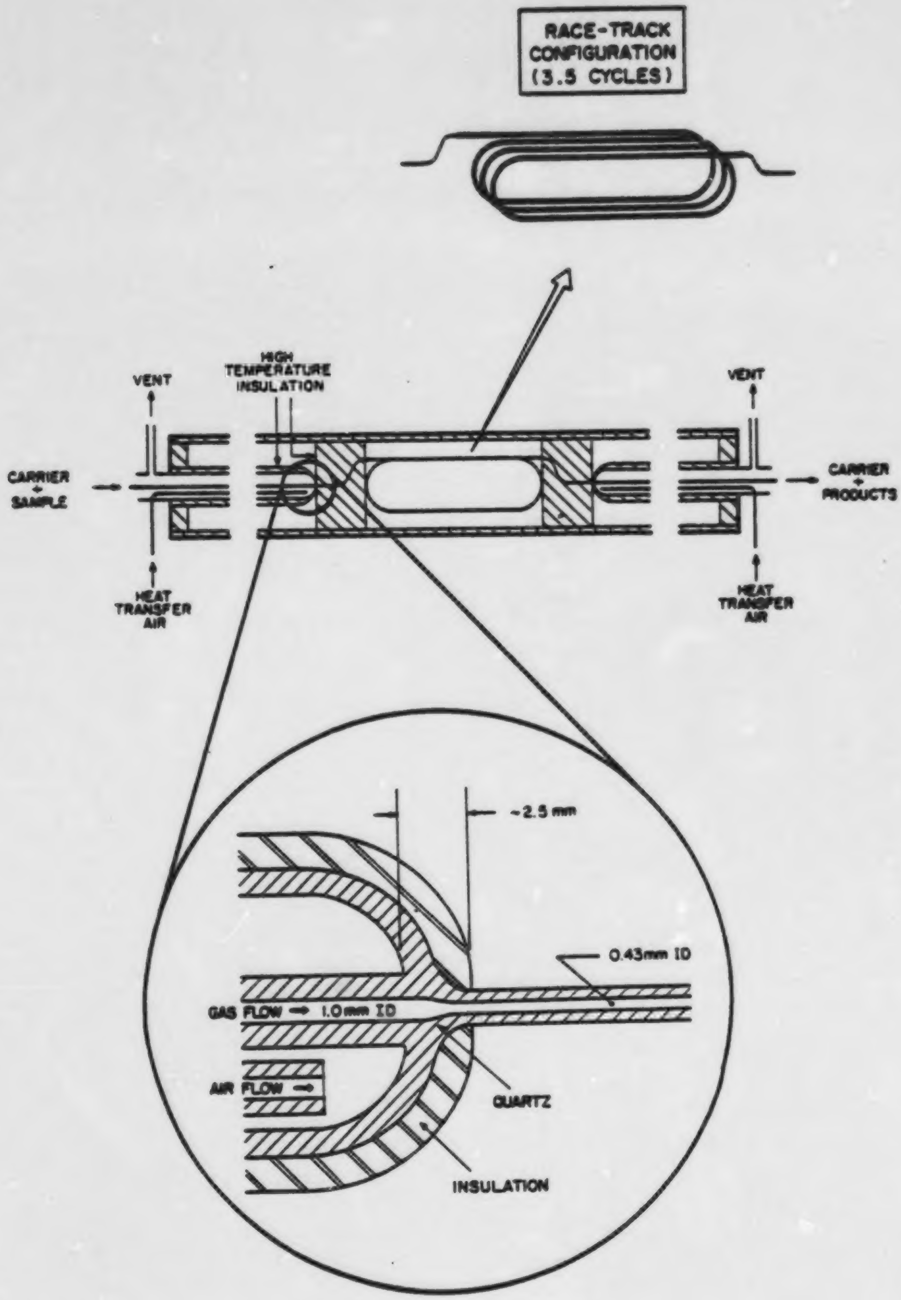

RACE-TRACK CONFIGURATION (3.5 CYCLES)
HIGH TEMPERATURE INSULATION
VENT
VENT
CARRIER + SAMPLE
CARRIER + PRODUCTS
HEAT TRANSFER AIR
HEAT TRANSFER AIR
~2.5 mm
0.43mm ID
GAS FLOW → 1.0mm ID
AIR FLOW →
QUARTZ
INSULATION

Figure 4.4. Additional Details of Reactor Assembly.

depending on the proximity of the transfer line to the reactor. At the reactor entry and exit points, the transfer lines constrict to a very fine bore providing increased gas velocity in these temperature transition regions. This reactor assembly enables a nearly square wave thermal exposure of sample molecules as illustrated in Figure 4.5. In addition, the residence times of molecules passing through this reactor is a narrow Gaussian distribution with 95% of molecules within ± 4% of the mean value. The mean residence time is therefore very representative of the time at temperature experienced by the sample.

Following the controlled exposure in the thermal reactor, the effluent is swept downstream to an in-line cryogenically cooled trap. This trap, shown in Figure 4.6, was packed with a glass wool trapping media and cooled by a counter-current flow of liquid and gaseous nitrogen. This trap serves as a holding station for condensible reactor effluent while a suitable gas chromatographic carrier gas displaces the decomposition atmosphere. After this gas exchange is completed, the trap is heated to liberate the captured products for transport to the analytical portion of the system.

Analyses on the TDAS are accomplished utilizing an LKB model 2091 gas chromatograph coupled mass spectrometer (GC-MS). This is an especially powerful analytical tool combining the separatory and the quantitative aspects of gas chromatography (GC) with the qualitative capabilities of mass spectrometry (MS).

The gas chromatograph is a modified Pye model 104. A high temperature gas switching valve attached to the side of the GC oven was utilized to by-pass the GC column during thermal decomposition, thus preventing attack of the GC separatory column liquid phase by low molecular weight volatile acids. For these analyses, a variety of open tubular columns were utilized with various temperature programs. However, due to a lack of subambient capability in this GC oven, the ability to trap and resolve low molecular weight species was impaired.

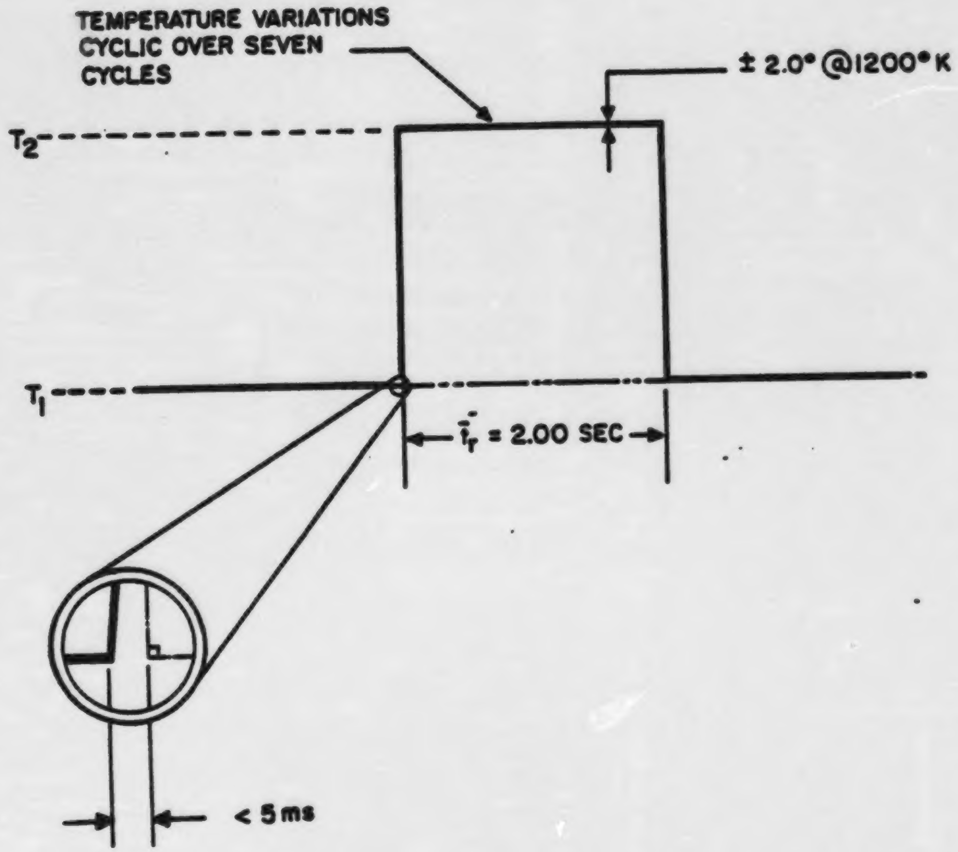
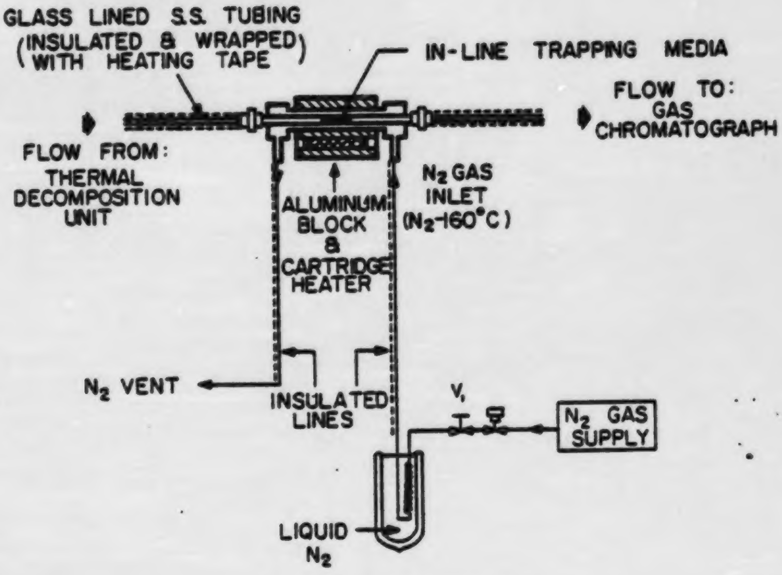

TEMPERATURE VARIATIONS CYCLIC OVER SEVEN CYCLES
± 2.0° @1200° K
T_2
T_1
$\bar{t}_r$ = 2.00 SEC
< 5 ms

Figure 4.5. Square Wave Profile of Gas-Phase Temperature Versus Time.

CRYOGENIC IN-LINE TRAP


GLASS LINED S.S. TUBING
(INSULATED & WRAPPED WITH HEATING TAPE)
IN-LINE TRAPPING MEDIA
FLOW TO: GAS CHROMATOGRAPH
FLOW FROM: THERMAL DECOMPOSITION UNIT
ALUMINUM BLOCK & CARTRIDGE HEATER
N_2 GAS INLET (N_2-160°C)
N_2 VENT
INSULATED LINES
V_1
N_2 GAS SUPPLY
LIQUID N_2

Trapping Mode:	Valve V_1 is open and trap temperature approaches: -160°C.
Desorb Mode:	Valve V_1 is closed and trap is subjected to a temperature program of -160° to +300°C at a pre-selected programming rate.

Figure 4.6. Schematic of Collection Trap Assembly.

When using thin film open tubular columns, the lowest molecular weight species which could be adequately trapped and resolved during this work was approximately 100 atomic mass units.

The mass spectrometer of the LKB system is a single focusing instrument with a 90° sector magnetic analyzer. Ions are generated using electron impact with energy adjustable from 5 to 100 eV with ionization currents in steps from 25 to 200 µA. Accelerating voltage is variable in four steps from 3.5 to 1.17 kV. The instrument was typically operated at 70 eV electron energy, 50 µA current, with 3.5 kV accelerating voltage. Resolution under these conditions was between 700 and 1,000 (10% valley).

There are two detectors in the mass spectrometer. A total ion current detector is used for generating a signal from the GC effluent which is ionized in the ion source. The output from this detector is displayed as a chromatogram by a potentiometric recorder. The other detector is an electron multiplier positioned at the terminus of the magnetic sector analyzer. Output from this detector provides mass spectra which can be displayed on a UV recording oscillograph or transmitted to a dedicated Digital Electronics Corporation PDP 11/04 Minicomputer. An LKB 2130 data system provides data acquisition and reduction routines while peripherals including a Tektronix 4012 graphics terminal and a Versatec 800 plotter enable display of data and results. In addition, a Texas Instruments Silent 700 ASR terminal is available to interface with external data bases (e.g., mass spectral and toxicological libraries) available through sources such as the NIH-EPA Chemical Information System.

4.2 PROCEDURES

In general, the experimental procedure for the TDAS is as follows:

First, the experimental conditions must be established. The appropriate reaction atmosphere must be selected (e.g., O_2, N_2, or various O_2 in N_2 combinations) and the corresponding high pressure gas plumbed into the system. The reactor temperature must be set and the mass flow controller adjusted to the appropriate value based on pressures, temperatures, reactor volume, and the desired mean residence time ($\bar{t}_r$). The cryogenic trap is cooled to approximately -40°C and the switching valve is set to by-pass the GC.

Next, the sample solution or neat sample is deposited on the appropriate insertion probe using a Hamilton microliter syringe. The solvent is allowed to evaporate and the probe is immediately placed in the insertion chamber. Once the probe is in place, the insertion region is heated at a preselected programmed rate resulting in thermal desorption of the sample from the probe into the flowing gas stream. The sample is subsequently swept through a heated transfer line into the reactor, through another heated transfer line, and into the cryogenic trap at which point condensible molecules are retained.

At this stage of the analysis, the reaction gas is purged by a GC suitable carrier gas and the switching valve positioned to place the GC in-line. The cryogenic trap is then heated at a programmed rate, liberating the sample from the trap so it may be swept downstream to be retained in the GC column inlet.

Next, the parameters for heating of the GC column are set and, depending upon the desired data, either a computer program is prepared to acquire mass spectral data or the total ion concentration detector and associated recorder are activated to obtain chromatographic data.

Extensive detail on the TDAS instrumentation and its operation, including calculation of flow parameters, may be found elsewhere.[7] Experimental details for specific compounds discussed in this report follow.

4.2.1 Five Component Aromatic Mixture

A test sample was prepared containing 2,6-dichlorobiphenyl, 2,2'-dibromobiphenyl, 2,7-dichlorodibenzo-p-dioxin, 2,8-dichlorodibenzofuran, and triphenylene. All compounds were obtained from RFR Corporation. Each of the five compounds was dissolved in toluene to a concentration of approximately 0.5 μg/μl. A Hamilton microliter syringe (Model 701) was used to inject 2.0 μl of the solution onto the sand-blasted probe and the solvent evaporated to dryness prior to insertion of the probe into the TDAS.

Chromatography was accomplished with a 15 m by 0.25 mm SE-30 silicone coated fused silica capillary column. The temperature program utilized for the GC oven was 30 to 230°C at 8°C per minute. Heilum carrier gas was used.

4.2.2 Biphenyl Mixture

A mixture of 2,6-dichlorobiphenyl and 2,2'-dibromobiphenyl was prepared using toluene for solvent. The concentration of each biphenyl in the solution was approximately 0.5 μg/μl. Both biphenyls were obtained from RFR Corporation.

Experiments were conducted using ten microliters of the solution injected onto the sand-blasted probe. The solvent was allowed to evaporate prior to insertion of the probe into the TDAS. The reaction gas was industrial grade compressed air supplied by Air Products and Chemicals, Inc.

Chromatographic separation was accomplished using a 15 m by 0.25 mm fused silica capillary column with an SE-30 silicone liquid phase. The column was obtained from J & W Scientific, Inc. A GC oven temperature program of 100 to 240°C at 8°C per minute and a helium carrier gas were used.

Mass spectra were obtained with an ion source temperature of 265°C, 70 eV electron energy, 50 μA trap current, and an accelerating voltage of 3.5 kV.

4.2.3 No. 2 Waste Stream

This sample was supplied by the US-EPA Project Officer. The sample as received was labeled Tank 2/C-0780-002. Analyses were conducted using a liquid fraction of the sample which was decanted from the particulate matter. Tests were conducted using 0.04 µl of this liquid injected onto the sandblasted probe. A Hamilton microliter syringe, model 7101 was used for these injections. Following injection, the probe was immediately placed within the insertion chamber.

Chromatographic separation was accomplished utilizing an SE-30 silicone coated 15 m by 0.25 mm fused silica capillary column. Helium was used as the carrier gas with detection by the total ion concentration detector. The temperature program for the GC analysis was from 30 to 230°C at 8°C per minute.

4.2.4 Chloroform

Chloroform (certified ACS) was obtained from Fisher Scientific Company. The test sample used for mass spectral analysis of thermal decomposition products was injected into the quartz wool packed probe and immediately inserted into the TDASinsertion chamber. The sample size was 0.1 1 of pure chloroform. The flowing reaction gas was industrial grade compressed air obtained from Air Products. The gas was dried using an in-line Hydro-Purge filter from Applied Science Laboratories.

Chromatographic separation of the thermal reaction products was made using a 15 m by 0.25 mm fused silica capillary column with as SE-30 silicon liquid phase. The column was obtained from J & W Scientific, Inc. Helium carrier gas was used. A temporary modification of the GC oven enabled subambient cooling of the column to approximately -25°C using liquid nitrogen. The column was then heated from -25°C to 0°C at an undetermined rate and from 0°C to 240°C at 10°C per minute. Mass spectra were obtained at 70 eV electron energy and 50 µA trap current with an accelerating voltage of 3.5 kV. The ion source temperature was 250°C.

4.2.5 Pentachloronitrobenzene (PCNB)

PCNB was obtained from the US-EPA Reference Standards Repository. The reported purity of this sample was 98+%. A sample was prepared for thermal decomposition studies by dissolving the PCNB in reagent grade toluene to a concentration of 1.8 µg/µl. Two microliters of this sample were injected onto the sand-blasted probe and the solvent allowed to evaporate to dryness prior to inserting the probe into the TDAS. The reaction gas was industrial grade compressed air from Air Products, and, dried using an in-line Hydro-Purge filter obtained from Applied Science Laboratories.

Chromatographic separation of the PCNB from its thermal reaction product was accomplished with a 15 m by 0.25 mm fused silica capillary column coated with an SE-30 silicone liquid phase. The column was obtained from J & W Scientific, Inc. Helium carrier gas was used.

Quantitative sample analyses were obtained using the total ion concentration detector. Mass spectra of the reaction product were obtained using 70 eV electron energy, 3.5 kV accelerating voltage, and 50 µA trap current at a source temperature of 265°C.

4.2.6 Polychlorinated Naphthalenes (PCNs)

A mixture of PCNs was obtained from RFR Corporation. This mixture of PCNs, Halowax 1001®, commercially distributed by Koppers Company, consists of approximately 50% chlorine by weight with the components averaging 250 amu in molecular weight. The test sample was prepared by dissolving 10 mg. of the mixture in 0.30 ml of acetone. This sample was then spiked with 1,2,3,4-tetrachloronaphthalene also obtained from RFR Corporation.

Chromatographic separation was accomplished on a 15 m by 0.25 mm SE-30 silicone coated fused silica capillary column. The GC oven was programmed from 100 to 240°C at 6°C per minute. Chromatograms were obtained using the total ion current detector.

4.2.7 2,2',4,5,5'-Pentachlorobiphenyl

This sample was obtained from RFR Corporation. It was dissolved in Nanograde® benzene from Mallinckrodt, Inc. to a concentration of 0.385 µg/µl. Three microliters of this solution were deposited on the sand-blasted probe and the solvent evaporated to dryness prior to insertion of the probe into the insertion chamber. Quantitative data were obtained using the total ion current detector.

4.2.8 Chlorobenzene Samples

All three chlorobenzenes tested in atmospheres containing various concentrations of oxygen were obtained from RFR Corporation. Individual samples were prepared as follows.

Hexachlorobenzene (HCBz)

A HCBz sample was prepared using Nanograde® toluene from Mallinckrodt, Inc. as the solvent. Two microliters of the 0.556 µg/µl solution were deposited on the sand-blasted probe and the solvent allowed to evaporate to dryness prior to insertion into the TDAS.

Pentachlorobenzene (PCBz)

Using Nanograde® toluene, PCBz was dissolved to a concentration of 0.798 µg/µl. Two microliters of this solution were deposited on the sand-blasted probe and the solvent evaporated to dryness prior to insertion.

1,2,3,4-Tetrachlorobenzene (1,2,3,4-TCBz)

Due to the increased volatility of 1,2,3,4-TCBz in relation to PCBz and HCBz, the quartz wool packed probe was used. A solvent of higher volatility than toluene was selected to insure complete evaporation of solvent. Pesticide grade methylene chloride from Fisher Scientific was used as the solvent with 1,2,3,4-TCBz dissolved to a concentration of 0.657 µg/µl. Two microliters of this solution was injected into the quartz wool and the solvent evaporated to dryness (for five minutes in an exhaust hood) prior to inserting the probe in the TDAS.

Air and oxygen were obtained from Air Products, while oxygen and nitrogen gas mixtures were obtained from and certified by the Specialty Gas Department of Air Products and Chemicals, Inc. A five minute purge period was utilized with these gases (after sample insertion but prior to heating of the sample chamber) to insure complete displacement of residual gases from the system prior to sample desorption and transport. All gases were dried using an in-line Hydro-Purge filter from Applied Science Laboratories. Quantitative data were obtained using the total ion current detector of the mass spectrometer.

4.2.9 Quality Control

Due to the wide range of physical properties exhibited by the compounds studied in this investigation, certain preliminary tests were required to insure reproducible sample input and transfer in the TDAS. This typically involved a "method development" period in which syringes, heating rates, and transfer temperatures were varied until a consistent (± 5%) sample transfer was demonstrated. The parameters established during the method development period were then utilized throughout the course of experimentation on the particular sample for which the method was developed.

In cases where quantitative data were obtained, changes in sample concentration with time (e.g. from loss of solvent) were corrected for by performing a daily non-degradative quantitation run. In addition to providing information as to the quantitative nature of the sample, this procedure also provided a check of the overall system performance on a daily basis.

SECTION 5

THE HIGH TEMPERATURE DESTRUCTION AND REACTION OF VARIOUS ORGANIC COMPOUNDS AND MIXTURES OF ORGANIC COMPOUNDS

5.1 FIVE COMPONENT AROMATIC MIXTURE

The relative thermal stabilities of a mixture of polycyclic aromatic compounds were established using the TDAS. These compounds, with aromatic centers linked by a variety of bond types and with variations in substitution, represent a broad cross section of polynuclear aromatic compounds. These compounds are listed and their structures shown in Table 5.1.

5.1.1 Results

The sequence of chromatograms shown in Figures 5.1-5.3 resulted from a series of thermal exposures in flowing air at a mean residence time ($\bar{t}_r$) of 2.0 seconds. At the lower exposure temperature (see Figure 5.1), the five major components of this mixture are clearly indicated along with several contaminants that were present in the 2,8-dichlorodibenzofuran stock. Figure 5.4 contains a compilation of the thermal decomposition data for each of the compounds based on quantitative reduction of the chromatograms.

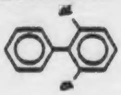
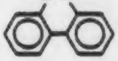
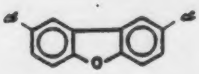
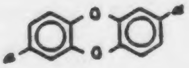
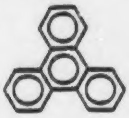
The effect of variation of $\bar{t}_r$ on the thermal decomposition of four of the five compounds was demonstrated at 750°C in flowing air. These data are listed in Table 5.2.

5.1.2 Discussion

The series of chromatograms and their associated thermal decomposition profiles indicate that in this mixture all of these aromatic compounds possess high thermal stabilities, with temperatures for 99.99 percent destruction in a range of 800-850°C. The least thermally stable of the compounds was triphenylene. The dibenzo-p-dioxin exhibited slightly greater thermal stability than triphenylene but less than the dibenzofuran and the biphenyls which exhibited nearly the same thermal stability.

TABLE 5.1

LIST OF COMPOUNDS IN FIVE COMPONENT AROMATIC MIXTURE

Compound	Structure	Empirical Formula
2,6-Dichlorobiphenyl		$C_{12}H_8Cl_2$
2,2'-Dibromobiphenyl		$C_{12}H_8Br_2$
2,8-Dichlorodibenzofuran		$C_{12}H_6O\ Cl_2$
2,7-Dichlorodibenzo-*P*-dioxin		$C_{12}H_6O_2Cl_2$
Triphenylene		$C_{18}H_{12}$

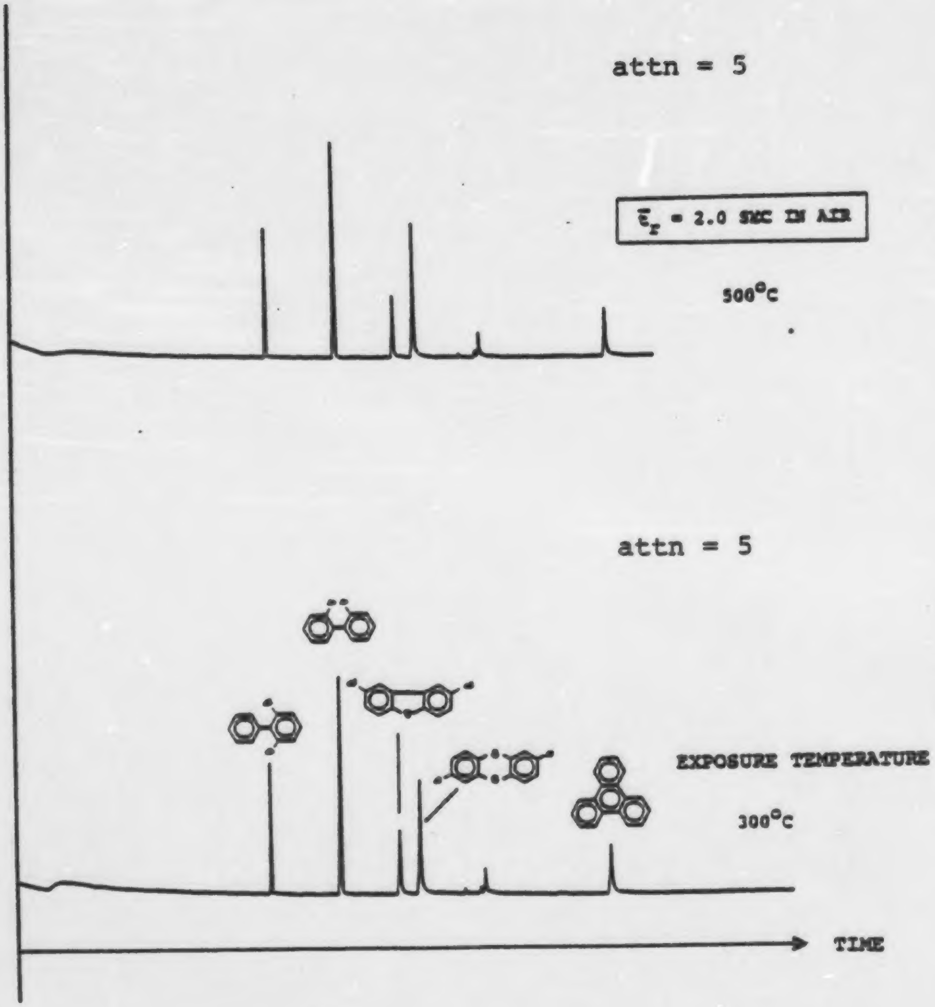


Figure 5.1. TDAS Tracings of Aromatic Mixture.

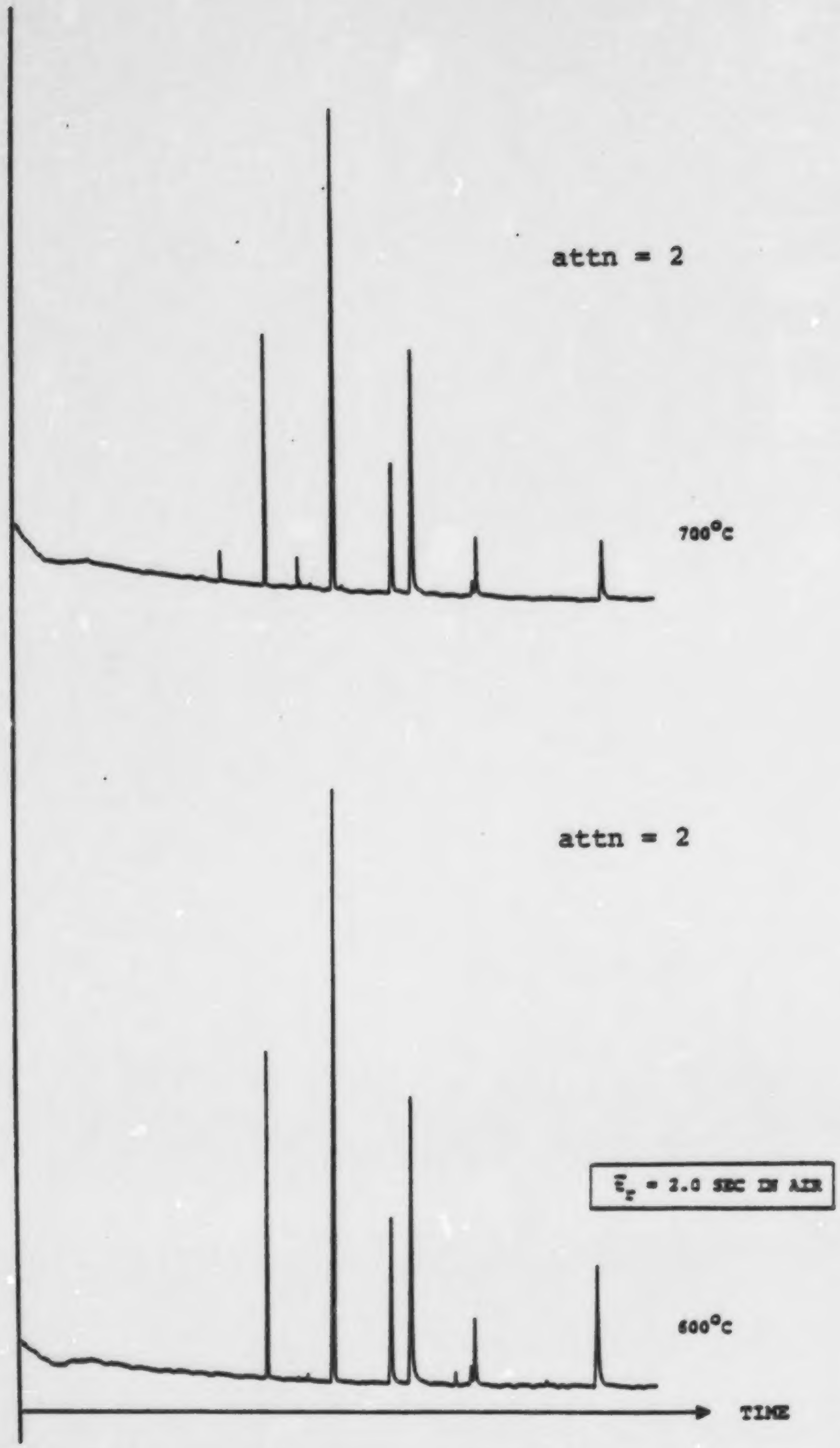


Figure 5.2. TDAS Tracings of Aromatic Mixture.

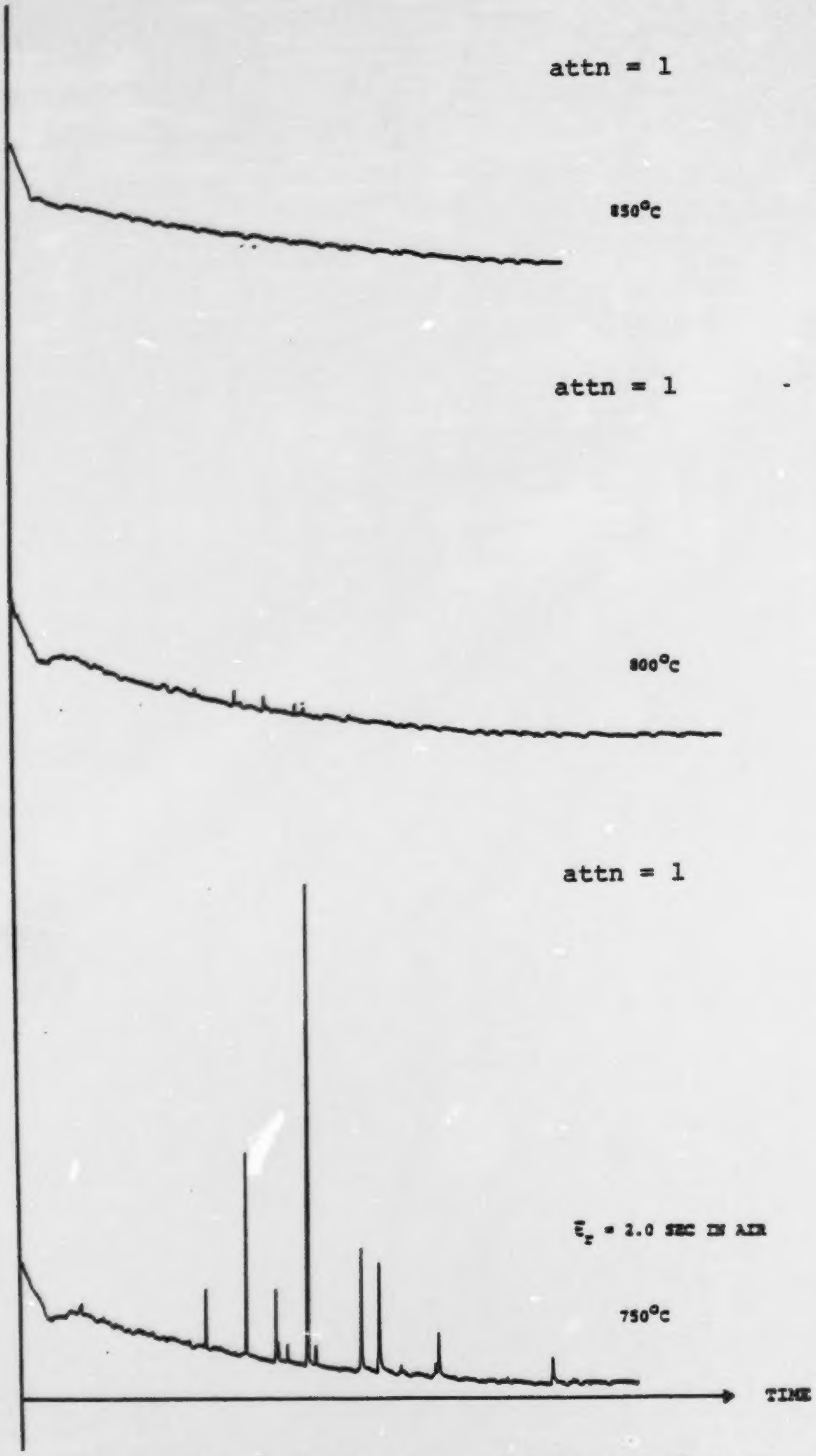


Figure 5.3. TDAS Tracings of Aromatic Mixture.

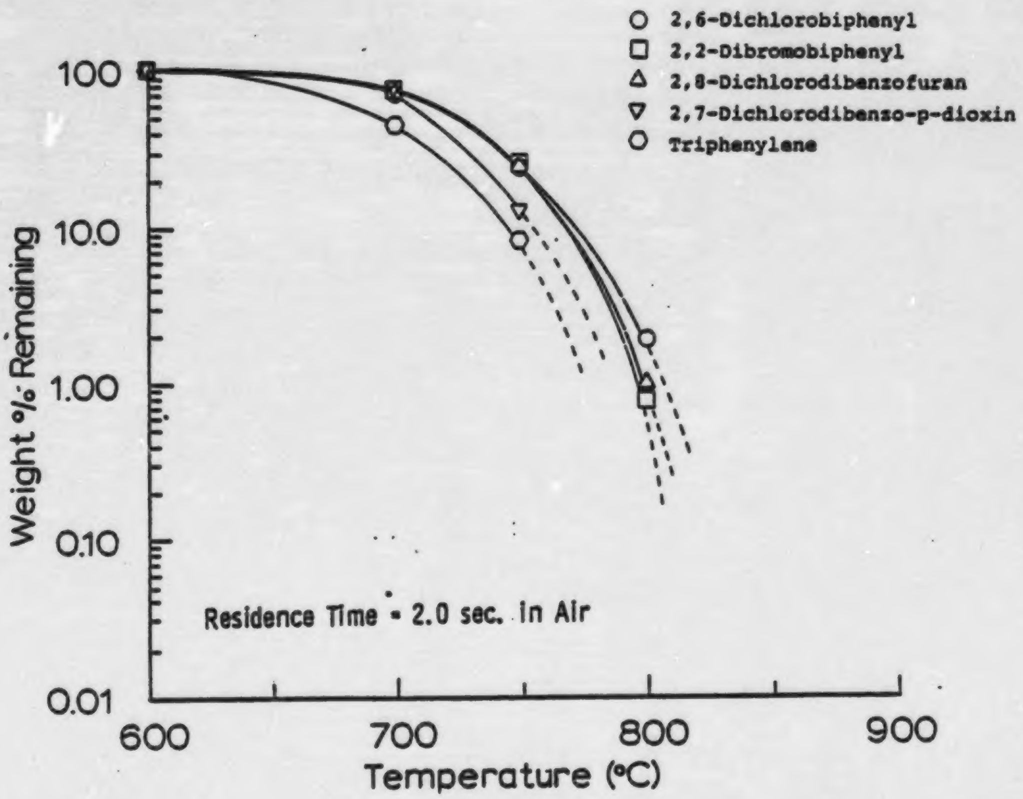


Figure 5.4. Compilation of Thermal Decomposition Profiles for Five Component Aromatic Mixture.

TABLE 5.2

WEIGHT PERCENT REMAINING AFTER 750°C EXPOSURE FOR RESPECTIVE MEAN RESIDENCE TIME*

Compound	Mean Residence Time, sec.			
	0.5	1.0	2.0	4.0
2,6-Dichlorobiphenyl	68.6	36.9	26.4	4.3
2,2'-Dibromobiphenyl	82.4	53.0	27.6	6.9
2,8-Dichlorodibenzofuran	85.3	51.6	26.5	3.9
2,7-Dichlorodibenzo-P-Dioxin	77.8	40.6	13.6	1.1

* in flowing air

Previous work by this laboratory[8] has indicated that electrophilic radical addition is a predominant destruction mechanism for some aromatics.

Based upon this assumption, one would expect the large planar triphenylene molecule to be the most thermally labile. Any electron deficiency created on this molecule as a result of such addition could be distributed across all four aromatic centers and thereby greatly stabilize the reaction intermediate and provide a low energy decomposition pathway.

The relative stability of the dichlorobiphenyl and the dibromobiphenyl may be due to a combination of effects. Since bromine is less electronegative than chlorine, its destabilizing effect on an intermediate such as that resulting from electrophilic addition would be less. The dibromobiphenyl, therefore, would be more amenable to this type of decomposition pathway than the dichlorobiphenyl. In addition, the carbon to bromine bond dissociation energy is approximately 14 kcal/mole less than the carbon to chlorine bond energy.[9] Therefore, any decomposition mechanism involving breaking of the carbon to halogen bond would also favor the dibromobiphenyl. It is entirely possible that the destruction of polybrominated biphenyls and polychlorinated biphenyls proceed by different mechanisms, carbon to bromine bond rupture in the former and electrophilic addition in the latter.

Interpretation of the relative stability of the dibenzo-p-dioxin and dibenzofuran is difficult due to the complex structure of these compounds. Inductive effects alone would favor electrophilic substitution in the dibenzofuran over the dibenzo-p-dioxin. However, twice as many stable resonance structures can be drawn for the dibenzo-p-dioxin intermediate which would make it more susceptible to electrophilic attack. The experimental data indicates that the resonance effects dominate.

Another pathway for decomposition is the rupture of the carbon to oxygen bond. Aliphatic ethers have carbon to oxygen bond energies of approximately 80 kcal/mole. If carbon to oxygen bond energies in the dibenzo-p-dioxin and dibenzofuran are similar, then this may be a major route for their destruction. The dibenzo-p-dioxin would be predicted to be slightly less stable simply because it has twice the number of carbon to oxygen bonds which are susceptible to rupture.

Table 5.2 shows the effect on thermal decomposition as a result of changing the $\bar{t}_r$ at 750°C in flowing air. (Triphenylene, due to its relatively low thermal stability, was not included in this analysis.) The four compounds shown all exhibit similar effects from variation of the $\bar{t}_r$. Increasing the residence time at temperature from 0.5 to 4.0 seconds decreased the average weight percent remaining for the four compounds from 79 percent at 0.5 sec. to 4.1 percent at $\bar{t}_r = 4.0$ seconds. Thus, the average destruction efficiency of 21 percent increases to an average destruction efficiency of greater than 95 percent by increasing the residence time at temperature.

Finally, it should be noted that several reaction products were produced by decomposition of this mixture in flowing air at 700 and 750°C. At 850°C all of the original components of the mixture as well as the PICs were destroyed to levels below the detection limit (approximately 0.01 percent).

5.2 BIPHENYL MIXTURE

Several stable PICs were observed during the thermal decomposition of the previously discussed five component mixture. Due to the well-established propensity of substituted biphenyl compounds to form thermal reaction products, it was anticipated that the 2,6-dichlorobiphenyl (DCB) and the 2,2'-dibromobiphenyl (DBB) were the major precursors to product formation from the five component mixture. A mixture of DCB and DBB was therefore prepared and subjected to tests using the TDAS.

5.2.1 Results

The reconstructed total ion current chromatogram showing the parent molecules and the thermal reaction products following exposure of the DCB/DBB mixture to 750°C for 2.0

seconds in flowing air is included as Figure 5.5. This plot represents the summation of ion currents detected at the multiplier versus scan number (defined as file position).

5.2.2 Discussion

The total ion current chromatogram developed for this DCB/DBB sample shows many similarities to the data shown previously (e.g., Figure 5.3) for the 750°C, 2.0 second exposure of the five component mixture. While the concentration of the DCB and DBB varied between the two samples analyzed, it appears that the predominant reaction products for both experiments are qualitatively similar. This would indicate that, as anticipated, the two substituted biphenyls were indeed the primary precursors of reaction products in the five component mixture analysis and that these products were formed relatively independent of the other components of the mixture. Figures 5.6-5.8 are mass histograms for the three identified products of incomplete combustion from the DCB/DBB mixture. These products exhibit a variety of bridging between their aromatic nuclei. The dibenzofuran has an ether linkage, possibly resulting from a hydroxy containing intermediate. Fluorenone has a keto linkage, possibly as a result of electrophilic attack by formyl radical and xanthenone exhibits a combination of both types of linkages. The xanthenone peak was not observed in the five component data. This may have been due to some dependence on the DCB/DBB concentration ratio or effects from the other three components.

The major unidentified doublet, centered on file position 130, showed evidence of being bromochlorobiphenyl isomers. Good spectra of these PICs could not be obtained, however indicators for both a disubstituted biphenyl and a bromochloro compound were present. Additional work would be required to substantiate this. However, this finding would be consistent with the rationale for the relative stability of the DCB and DBB discussed in 5.1.2.

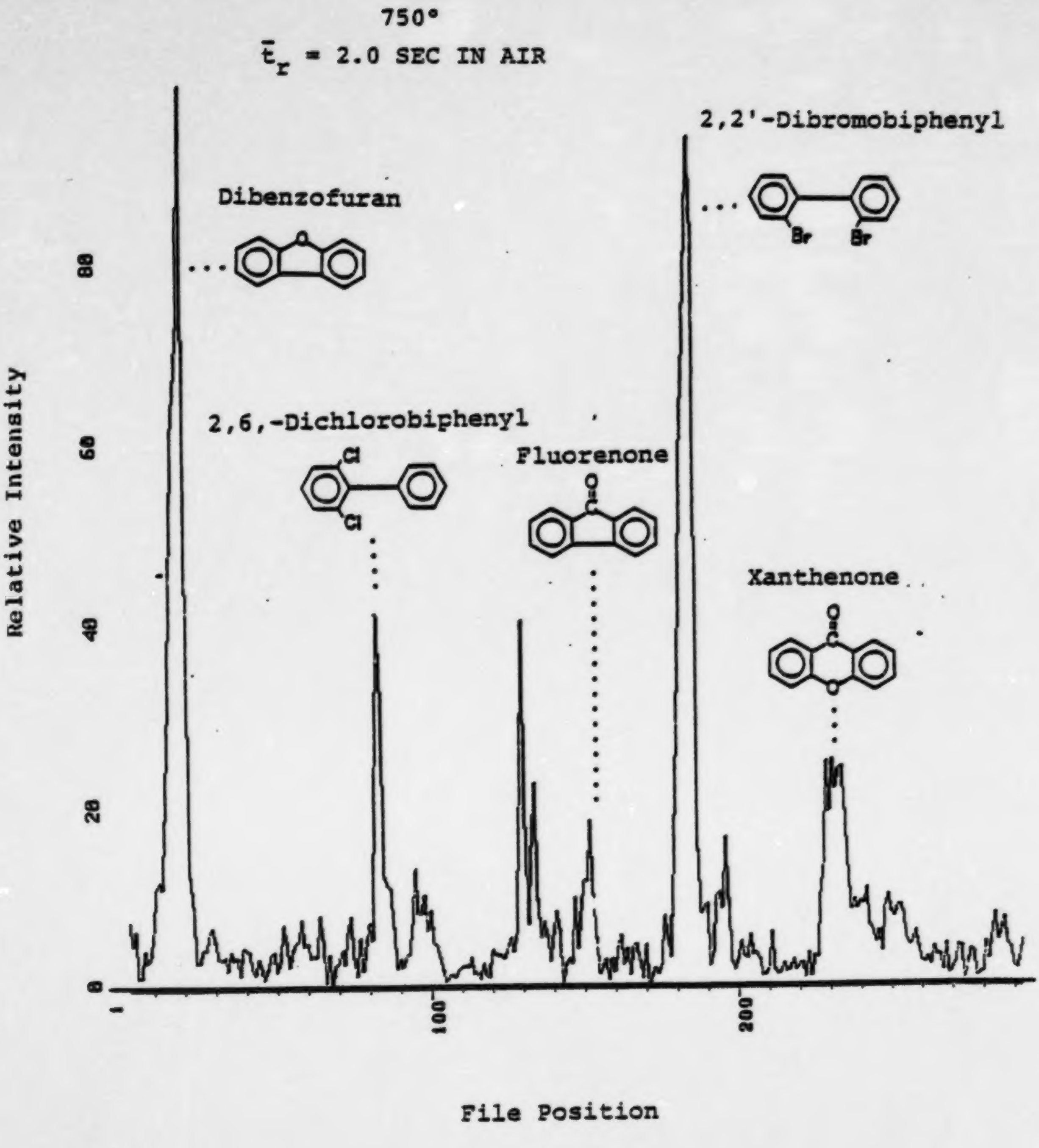


Figure 5.5. Reconstructed Total Ion Chromatogram for DCB/DBB Mixture and Their Reaction Products.

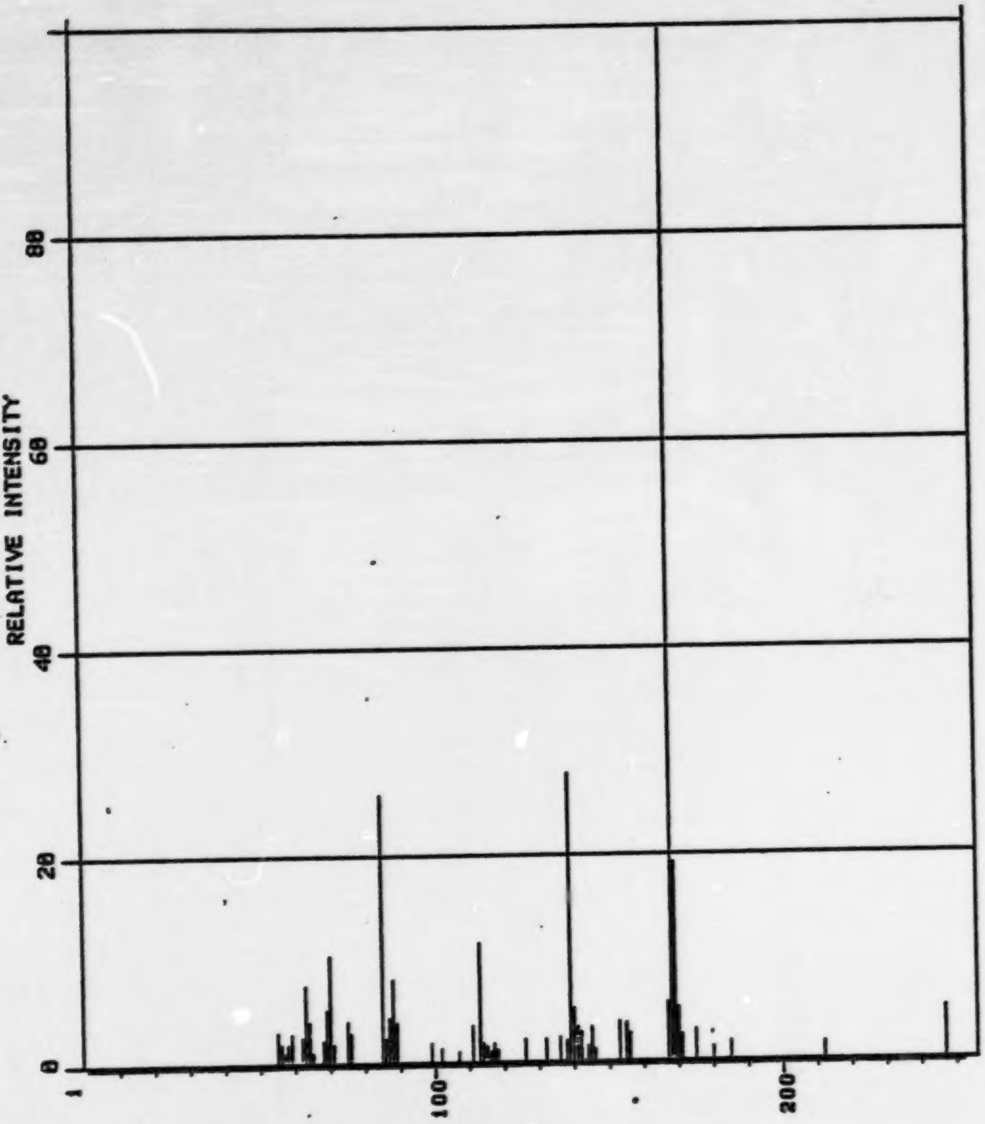


Figure 5.6. Mass Histogram of Reaction Product Identified as Dibenzofuran.

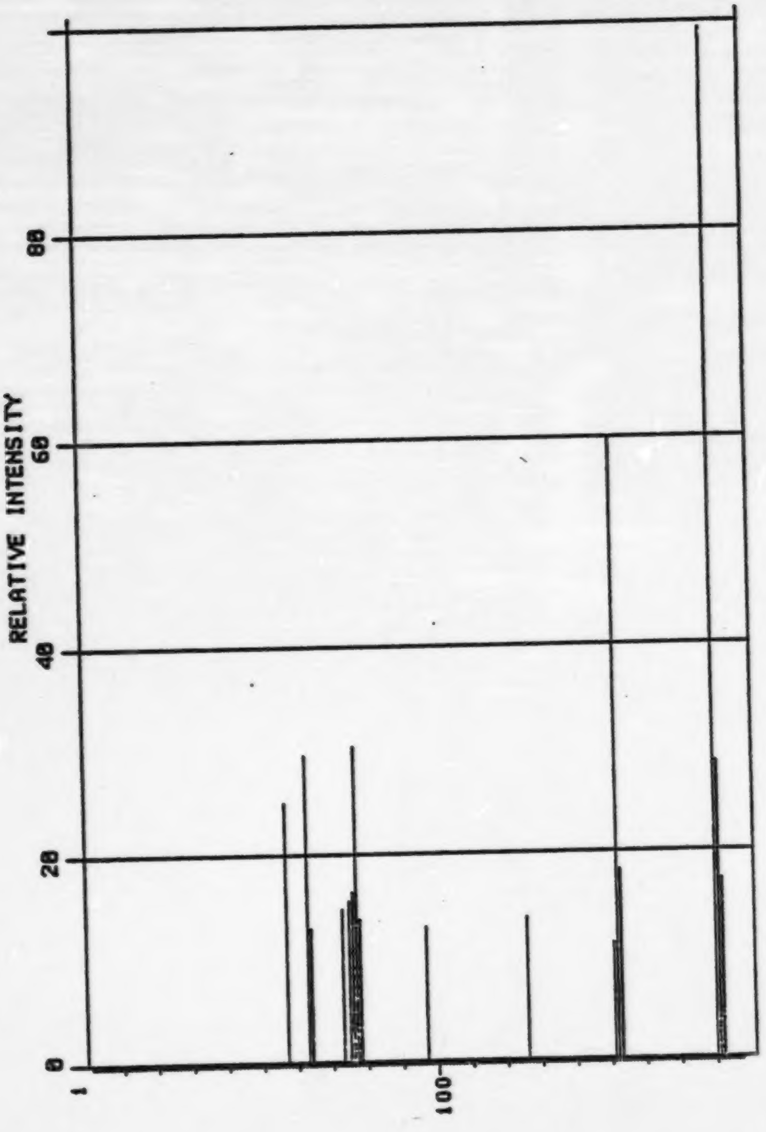


Figure 5.7. Mass Histogram of Reaction Product Identified as Fluorenone.

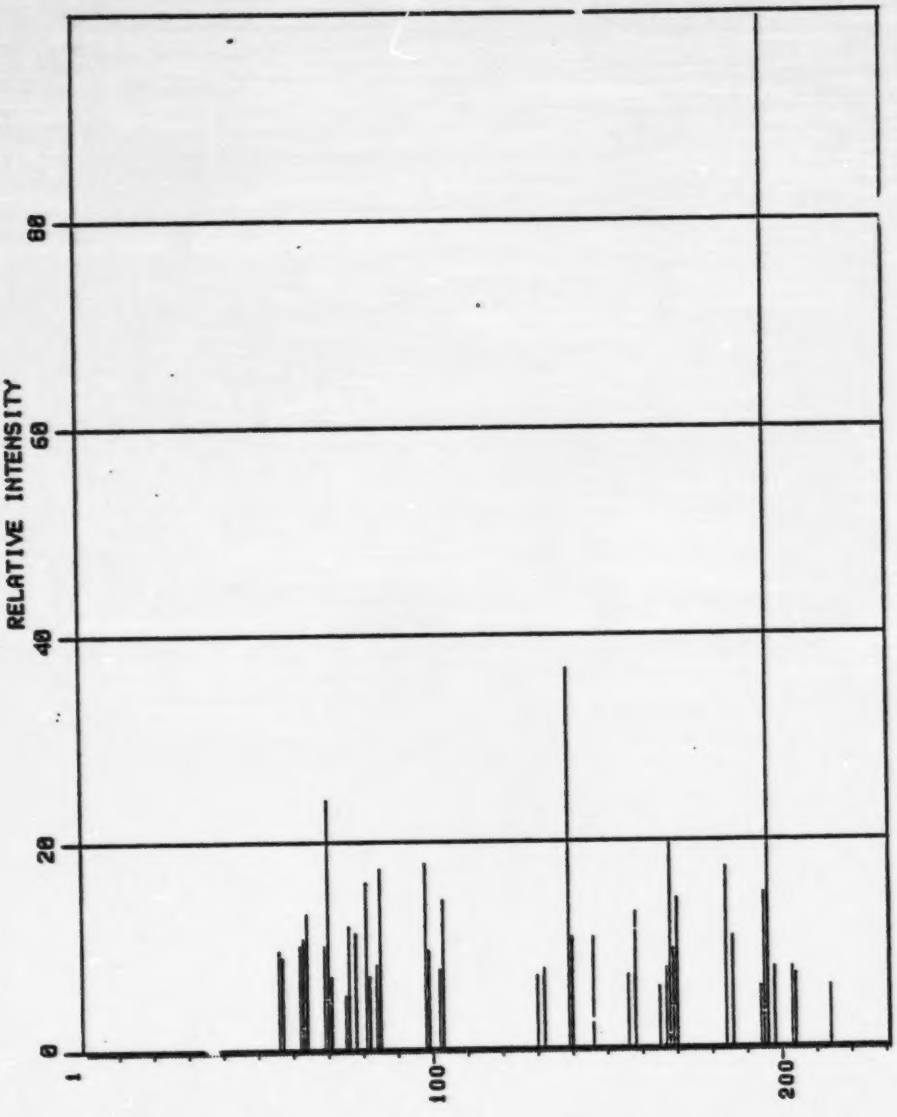


Figure 5.8. Mass Histogram of Reaction Product Identified as Xanthenone.

5.3 NO. 2 WASTE STREAM

A complex industrial waste mixture was thermally profiled using the TDAS. This mixture was supplied by the US-EPA Project Officer and was labeled as being from Tank 2/6-0780-002.

5.3.1 Results

Figures 5.9 and 5.10 show the gas chromatographic tracings which resulted from a series of thermal decomposition tests in which the No. 2 waste stream sample was subjected to various temperatures for 2.0 seconds in flowing air. Two substances were selected from this very complex mixture and quantitatively analyzed. These two substances were considered fairly representative of the thermal decomposition behavior of the entire sample. Profiles for the thermal decomposition of the selected components are plotted in Figure 5.11.

5.3.2 Discussion

As demonstrated by the sequence of chromatograms, except for low levels of some volatile species, the waste stream has been successfully destroyed at 800°C. In fact, significant decomposition begins at 500°C as evidenced by the decreased concentration of compound "B" as well as the increased magnitude of the volatile products of incomplete combustion (PICs).

The presence of volatile PICs brings to light an important limitation of the TDAS. While capillary columns provide state-of-the-art resolution of complex organic mixtures, without subambient temperature programming capability, the resolution of organics of low molecular weight (e.g., <100 amu) is unsatisfactory. Since the Pye Model 104 GC oven on the TDAS lacked subambient capability and a capillary column was in use, the resolution and identification of low molecular weight PICs (such as those detected at 500°C) was impossible.

5.4 CHLOROFORM

A temporary modification of the Pye GC oven was made which would enable subambient cooling of the capillary column. A

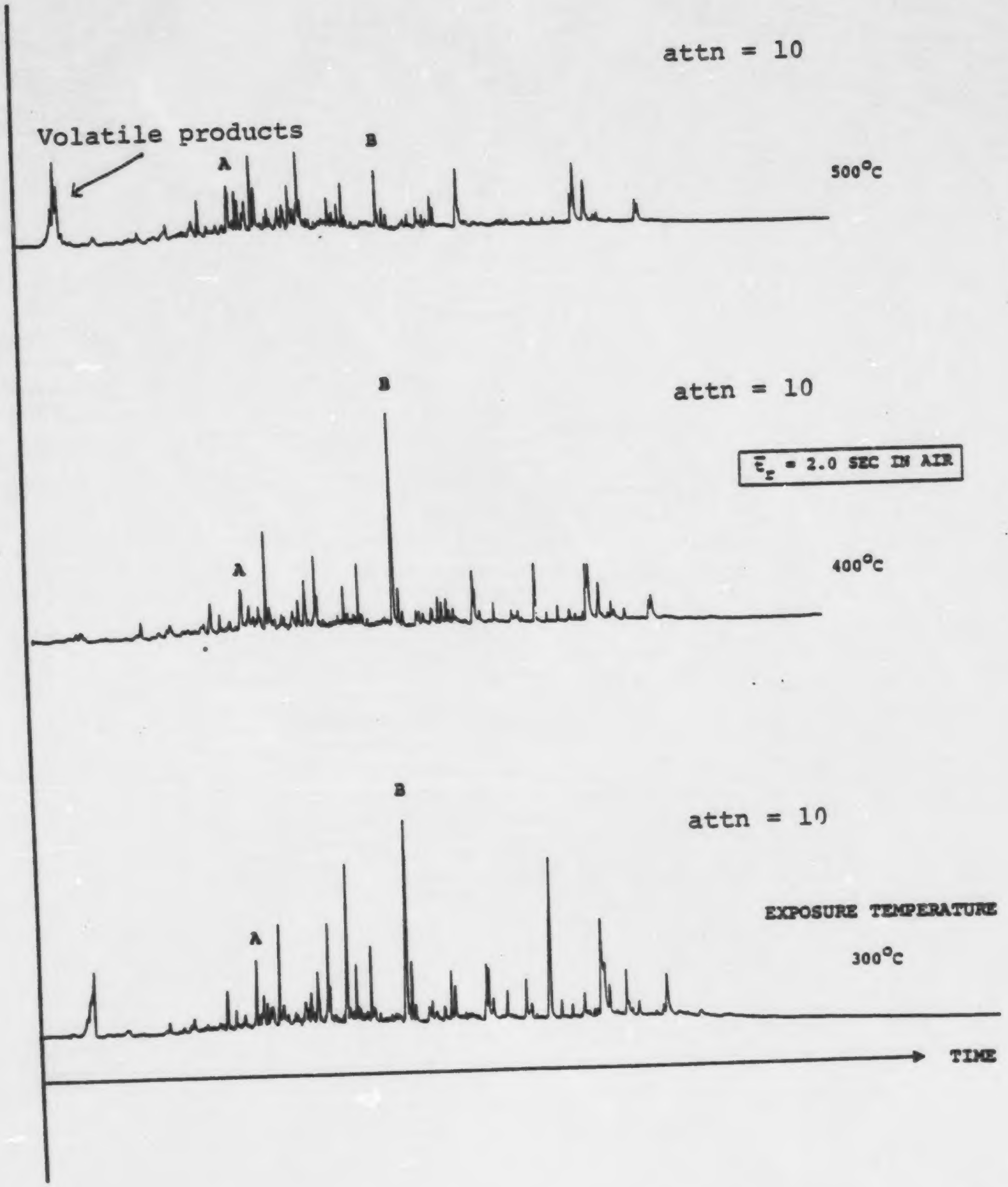


Figure 5.9. GC Tracings for No. 2 Waste Stream Sample.

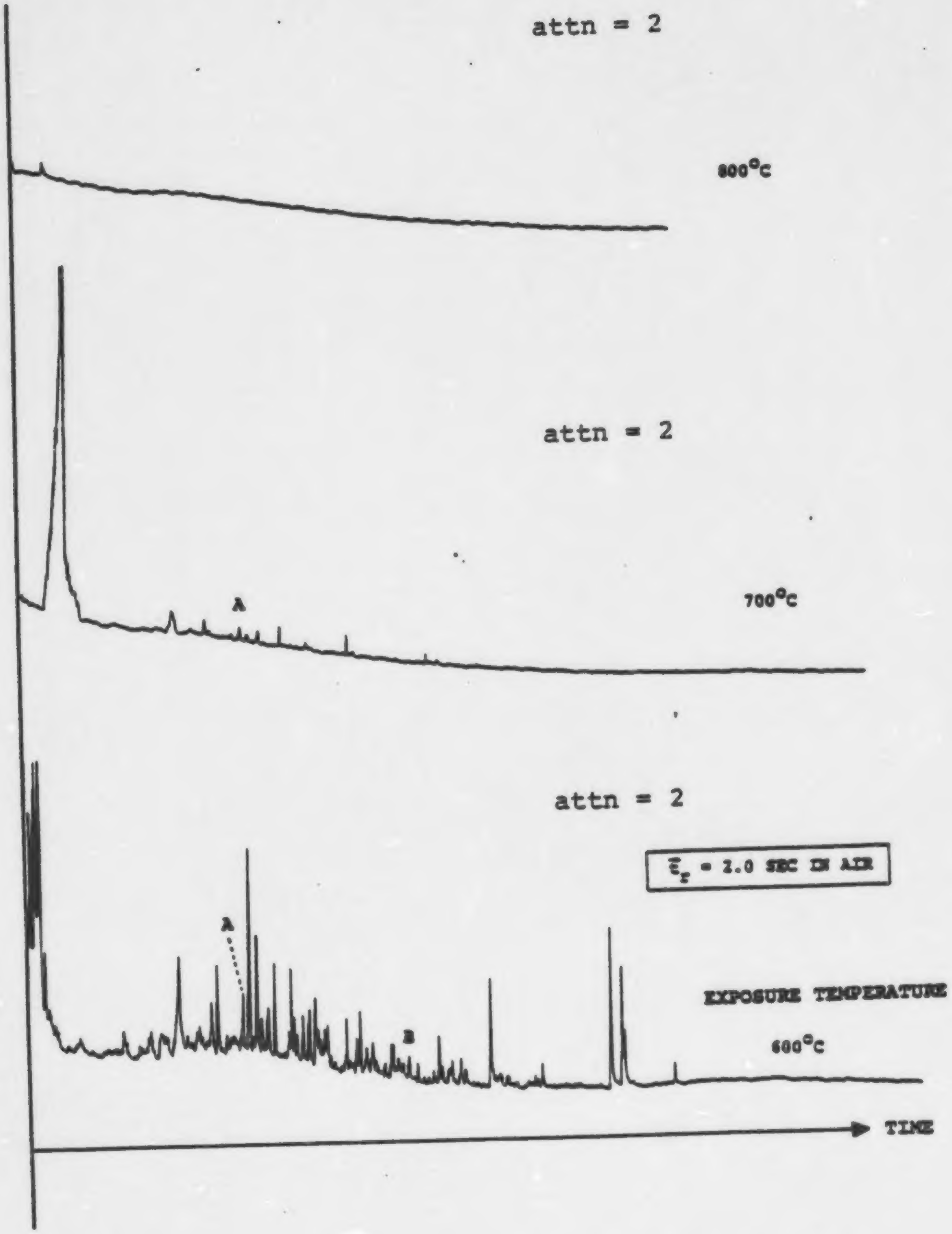


Figure 5.10. GC Tracings for No. 2 Waste Stream Sample.

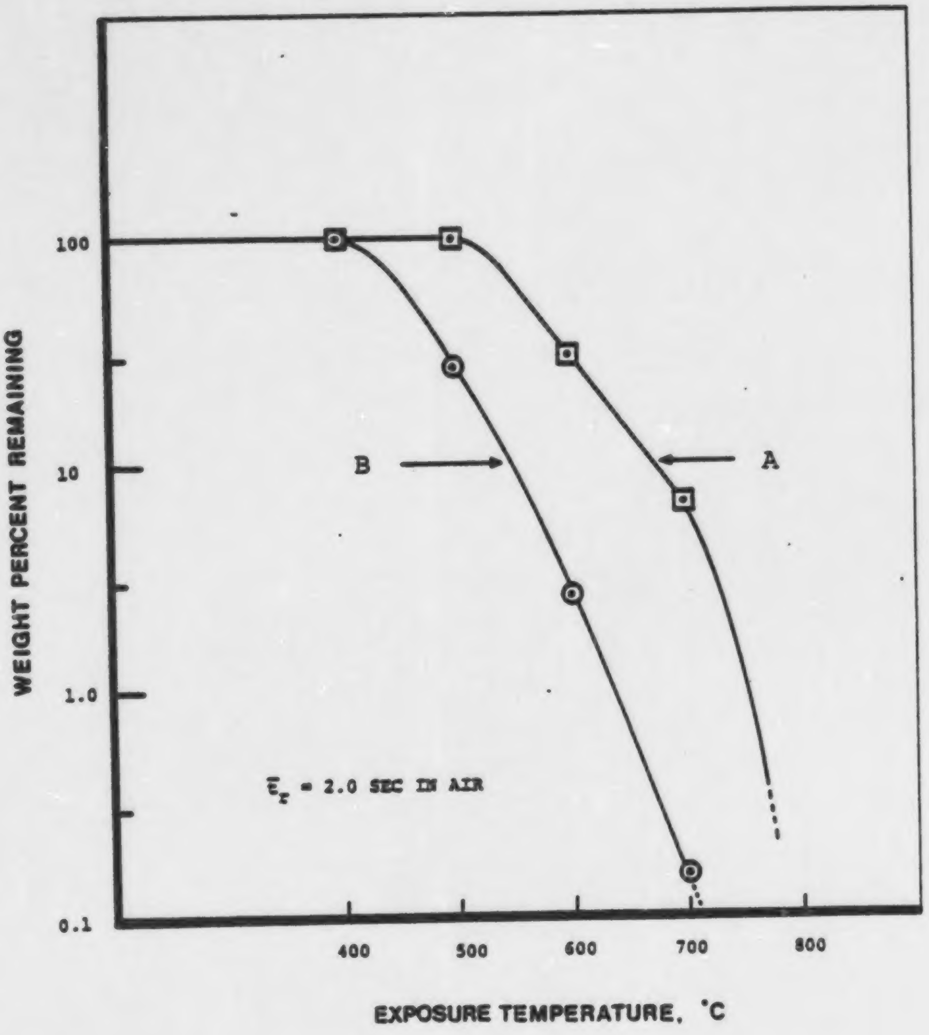


Figure 5.11. No. 2 Waste Stream Thermal Decomposition Profiles.

thermal decomposition study of a volatile chlorinated organic was undertaken to test the methodology associated with the modification. Chloroform was selected because it is a hazardous compound and there was interest as to the propensity of a single carbon chlorinated specie to form reaction products.

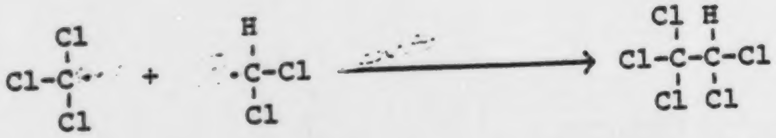
5.4.1 Results

Chloroform was exposed to 600°C for 2.0 seconds in flowing air using the TDAS. A reconstructed total ion current chromatogram of the reaction products is shown in Figure 5.12. Mass histograms of the products are included as Figures 5.13 and 5.14.

5.4.2 Discussion

Relative to the previously discussed halogenated biphenyls and naphthalenes, chloroform is a thermally labile compound. No chloroform was detected following exposure to 600°C in flowing air for 2.0 seconds. However, as shown in Figure 5.12, this compound does have a high propensity to form PICs, and these reaction products have good survivability at the temperature at which they are formed.

Figures 5.13 and 5.14 are mass histograms of the tentatively identified products. Confirmation of these products requires favorable comparison of retention data as well as mass spectra. Since the subambient capability of the GC oven was only a temporary modification, there was no subambient temperature programming capability. The reproducibility of heating rates and, therefore, retention data was poor and, as a consequence, not useful for confirmatory purposes. In any case, the reaction products proposed would be anticipated, pentachloroethane as the result of a bimolecular reaction of trichloromethyl and dichloromethyl radicals



$$\mathrm{Cl_3C\cdot + \cdot CHCl_2 \longrightarrow Cl_3C{-}CHCl_2}$$

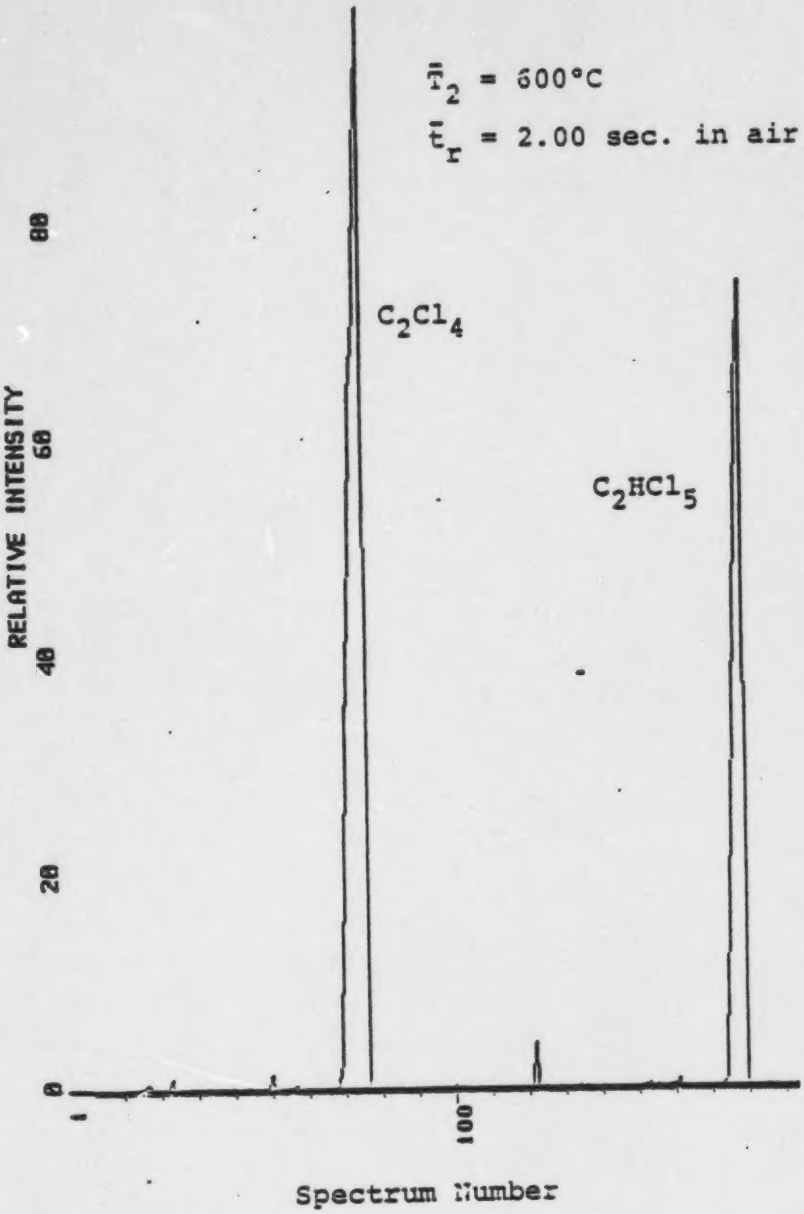


Figure 5.12. Reconstructed Total Ion Chromatogram of Products Resulting From Thermal Exposure of Chloroform.

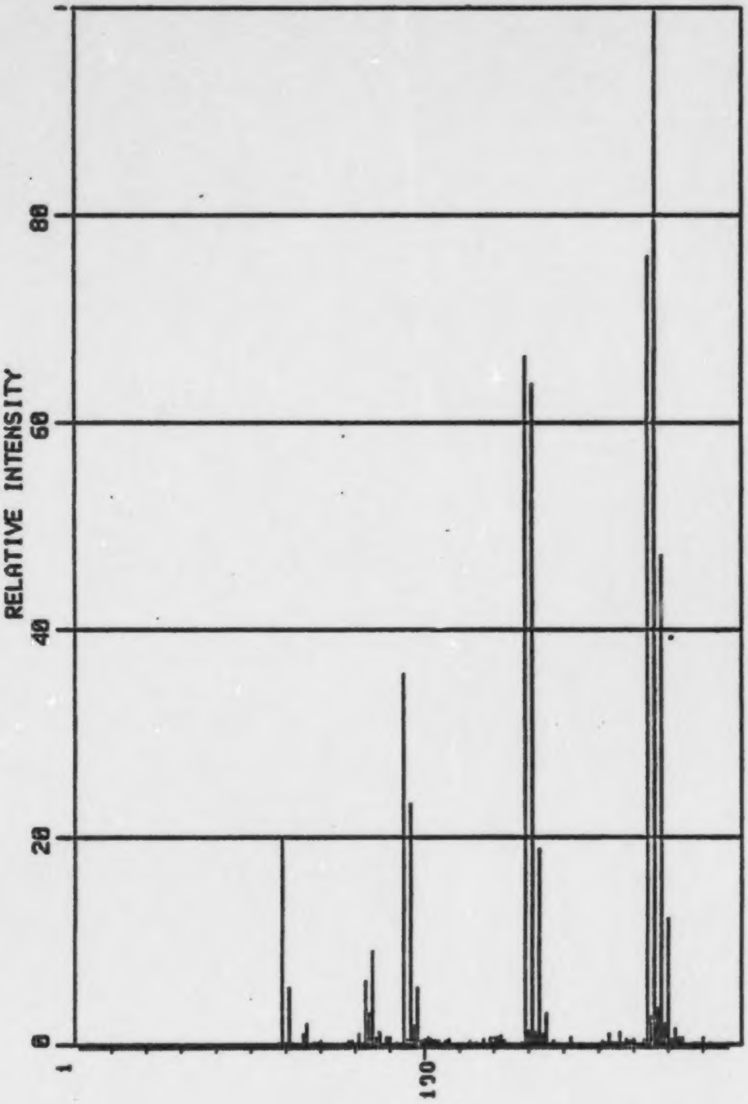


Figure 5.13. Mass Histogram of Thermal Reaction Product Tentatively Identified as Tetrachloroethylene.

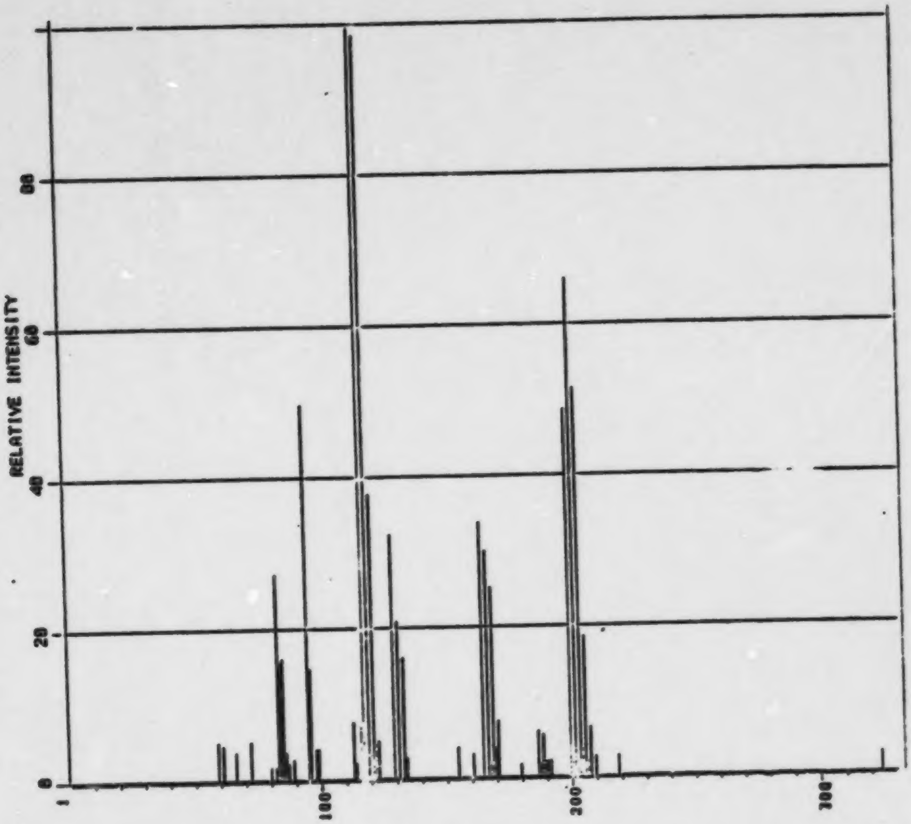
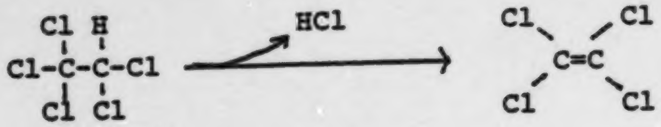


Figure 5.14. Mass Histogram of Thermal Reaction Product Tentatively Identified as Pentachloroethane.

and tetrachloroethylene as the result of the concerted elimination of HCl.



5.5 PENTACHLORONITROBENZENE

Pentachloronitrobenzene (PCNB) is distributed worldwide as a fungicide[10] and is included on the Appendix VIII List of Hazardous Constituents[11]. Based on the heat of combustion method for ranking incinerability, PCNB (1.62 kcal/gram) would be ranked among the top ten percent of the compounds from the Appendix VIII list in terms of difficulty to incinerate. Therefore, the thermal decomposition characteristics of this compound were of interest and were determined using the TDAS.

5.5.1 Results

The thermal decomposition profile for PCNB in flowing air at a mean residence time of 2.0 seconds is included as Figure 5.15. While obtaining this data, a major thermal reaction product was observed. This PIC was identified as hexachlorobenzene (HCBz) and confirmed using an analytical standard for comparison of spectra and retention data. Chromatograms illustrating the PCNB destruction and HCBz formation are shown in Figure 5.16 with the thermal profiles for both substances quantified in Figure 5.17.

5.5.2 Discussion

As shown in Figure 5.15, 99.99 percent of the PCNB experiencing a 2.0 second mean residence time in flowing air will be destroyed at 590°C. Despite the low heat of combustion for this compound, it is the most thermally fragile compound which is described in this report. Of twenty other Appendix VIII compounds for which thermal decomposition data has been recently reported[8], none exhibited lower thermal stability than PCNB.

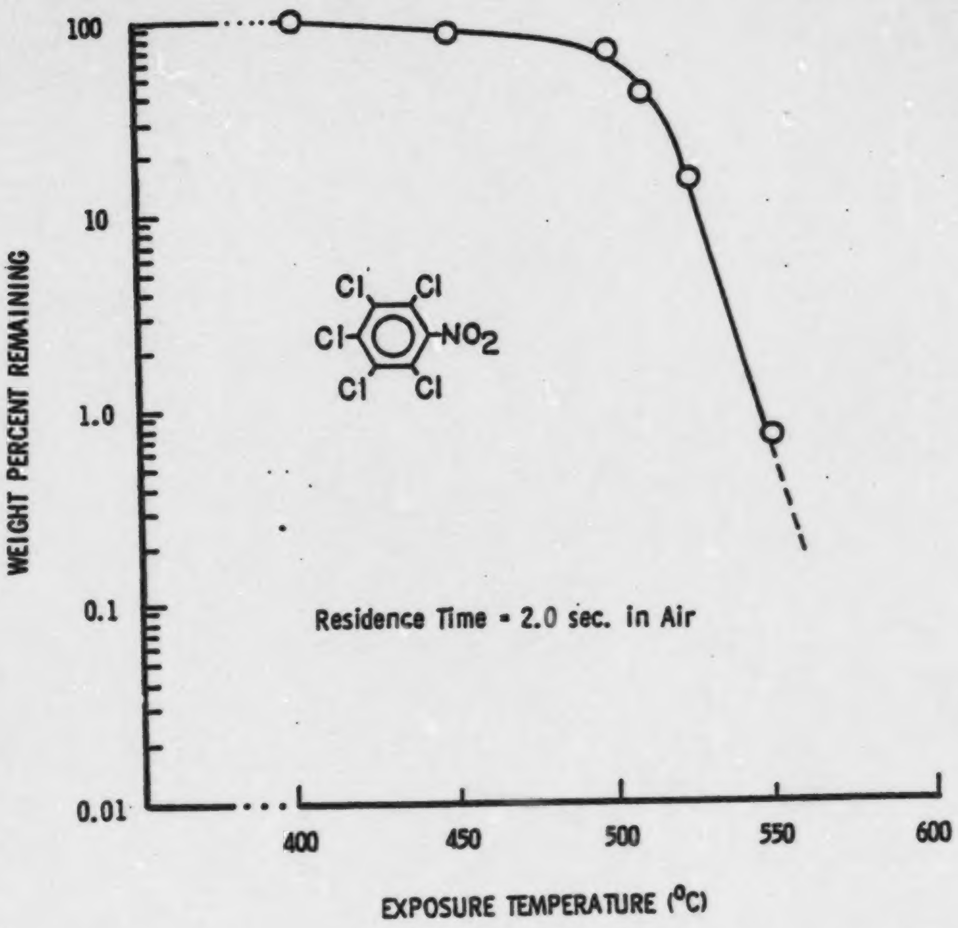


Figure 5.15. Thermal Decomposition Profile of PCNB.

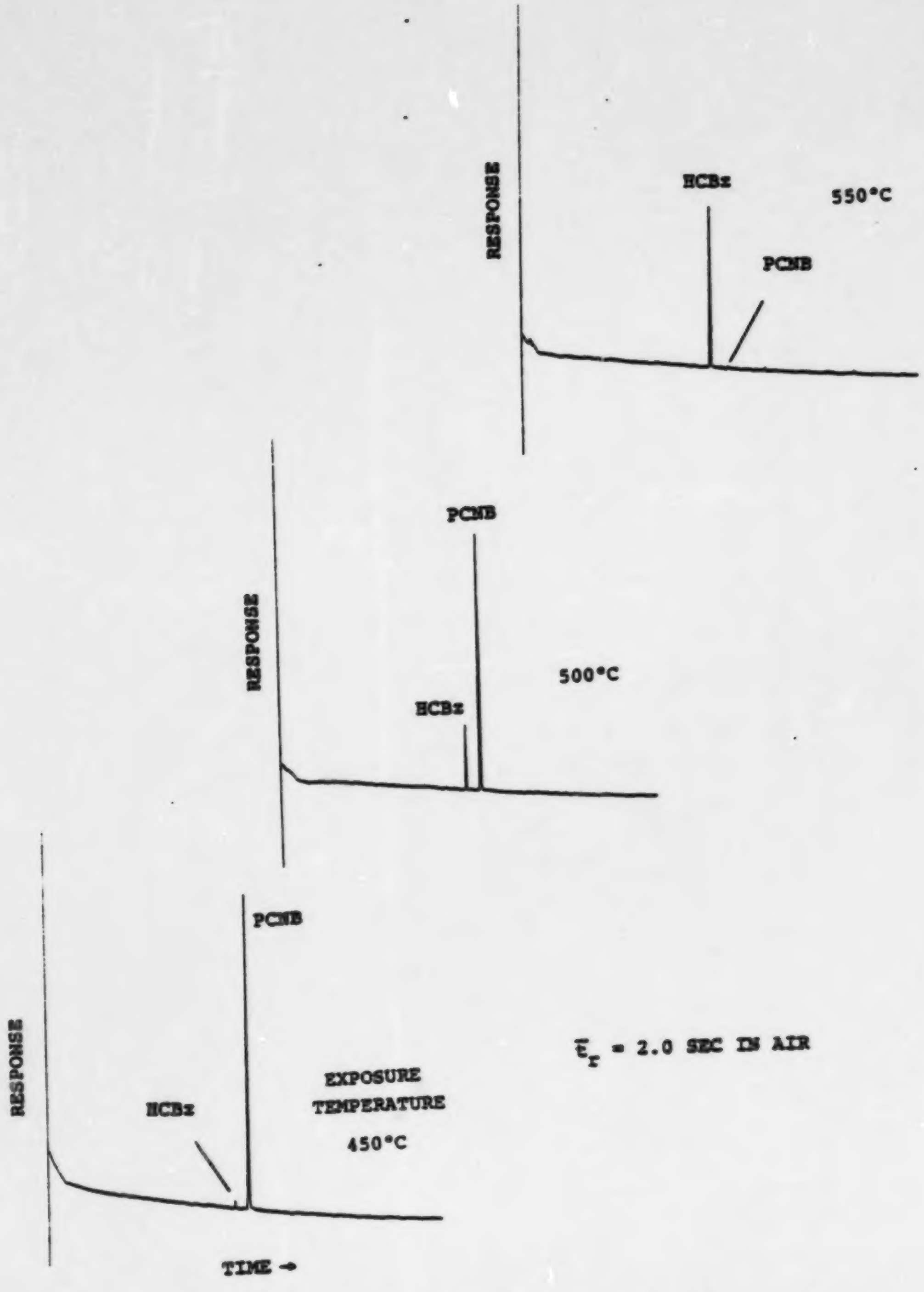


Figure 5.16. TIC Detector Output Signal Tracings Showing Thermal Decomposition of PCNB and Formation of HCBz.

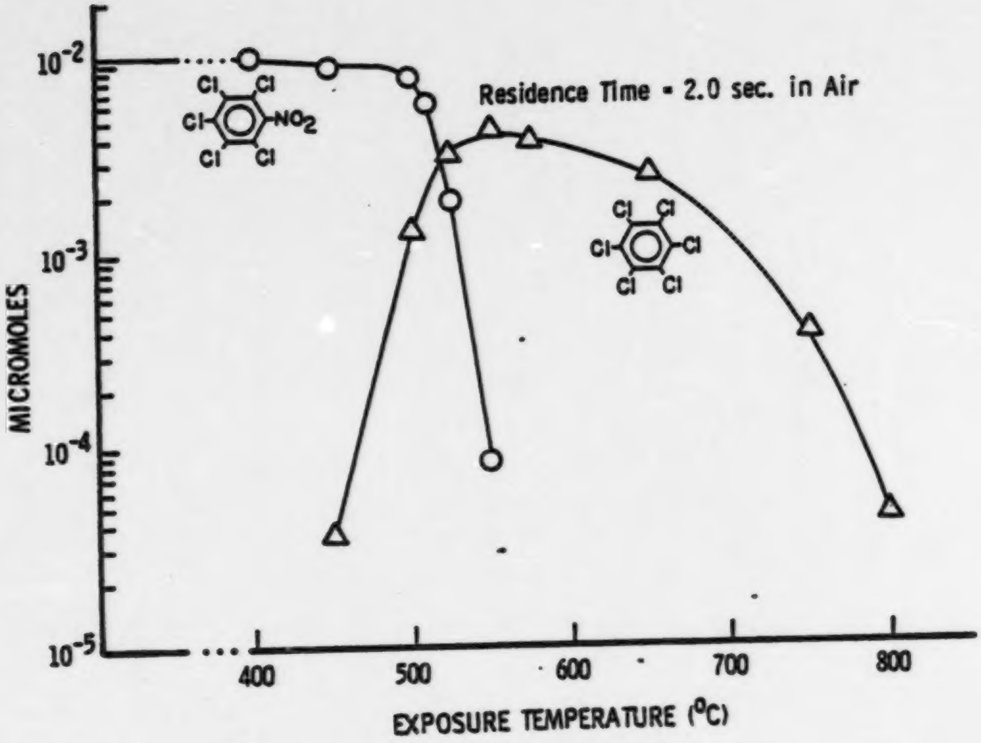


Figure 5.17. Quantitative Thermal Profiles for PCNB and HCBz.

In Figure 5.17, it can be seen that the region of maximum product formation occurs at the temperature required for 99.99 percent destruction ($T_{99.99}$) of the parent compound. This same phenomenon was reported[5] previously for the thermal decomposition of the pesticide DDT. In both cases, destruction of the thermal reaction product required temperatures more than 200°C higher than the $T_{99.99}$ of the parent compound.

The yield of HCBz from PCNB exceeds 30 percent at 575°C. A possible pathway for the HCBz formation is as follows: the carbon to nitrogen bond in PCNB is intrinsically weak (70 kcal/mole in nitrobenzene)[8] and is further weakened by the inductive effects of the chlorine substituents on the ring. Cleavage of this bond would yield a pentachlorophenyl radical which could further decompose or react with a chlorine atom. The absence of hydrogen on the parent PCNB and in the flowing gas stream (H_2O is purged from the air) would promote the availability of chlorine atoms for such a reaction to occur. Another possible product of such a pathway would be decachlorobiphenyl, a compound which is also very thermally stable. This compound was not observed in the chromatograms; however, the column temperature and elution time were insufficient to elute this high-molecular weight compound even if it was present.

5.6 POLYCHLORINATED NAPHTHALENES

Polychlorinated naphthalenes (PCNs) are used for a variety of applications including plasticizers, protective coatings, sealing compounds, crankcase additives, penetrating oils, fire retardants, and as electrical insulating materials. A commercial mixture of PCNs containing approximately 50 percent by weight chlorine was obtained, spiked with 1,2,3,4-tetrachloronaphthalene, and subjected to a series of tests using the TDAS.

5.6.1 Results

Figures 5.18 and 5.19 show a series of chromatograms resulting from a sequence of experiments in which the PCNs

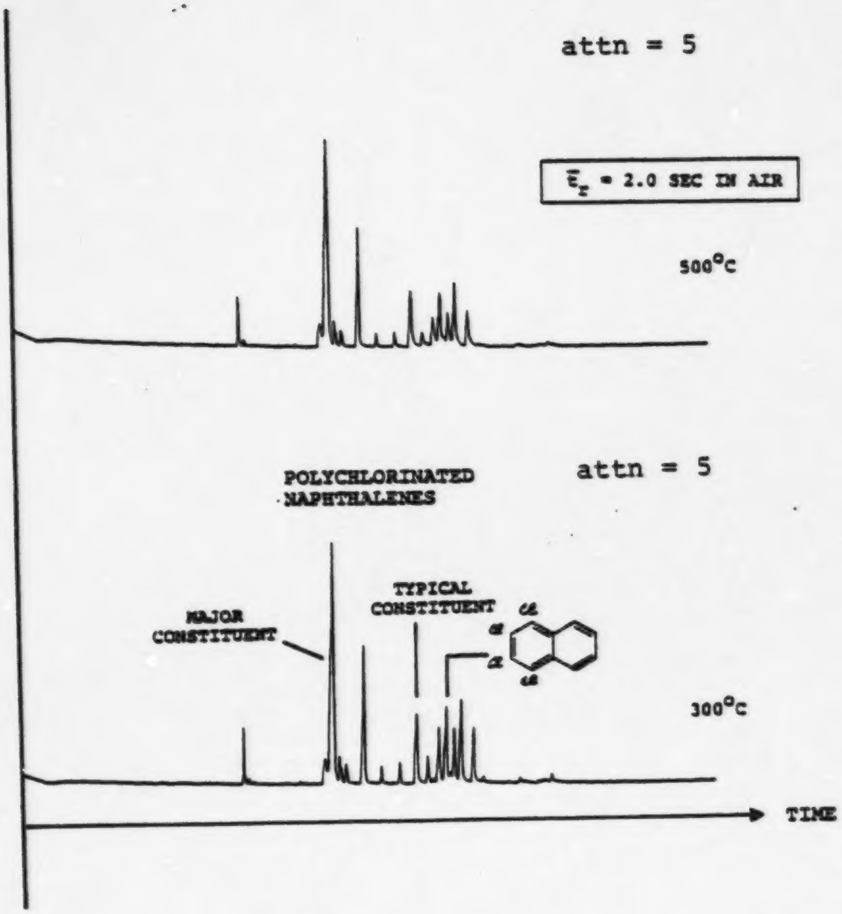


Figure 5.18. Halowax TDAS Tracings.

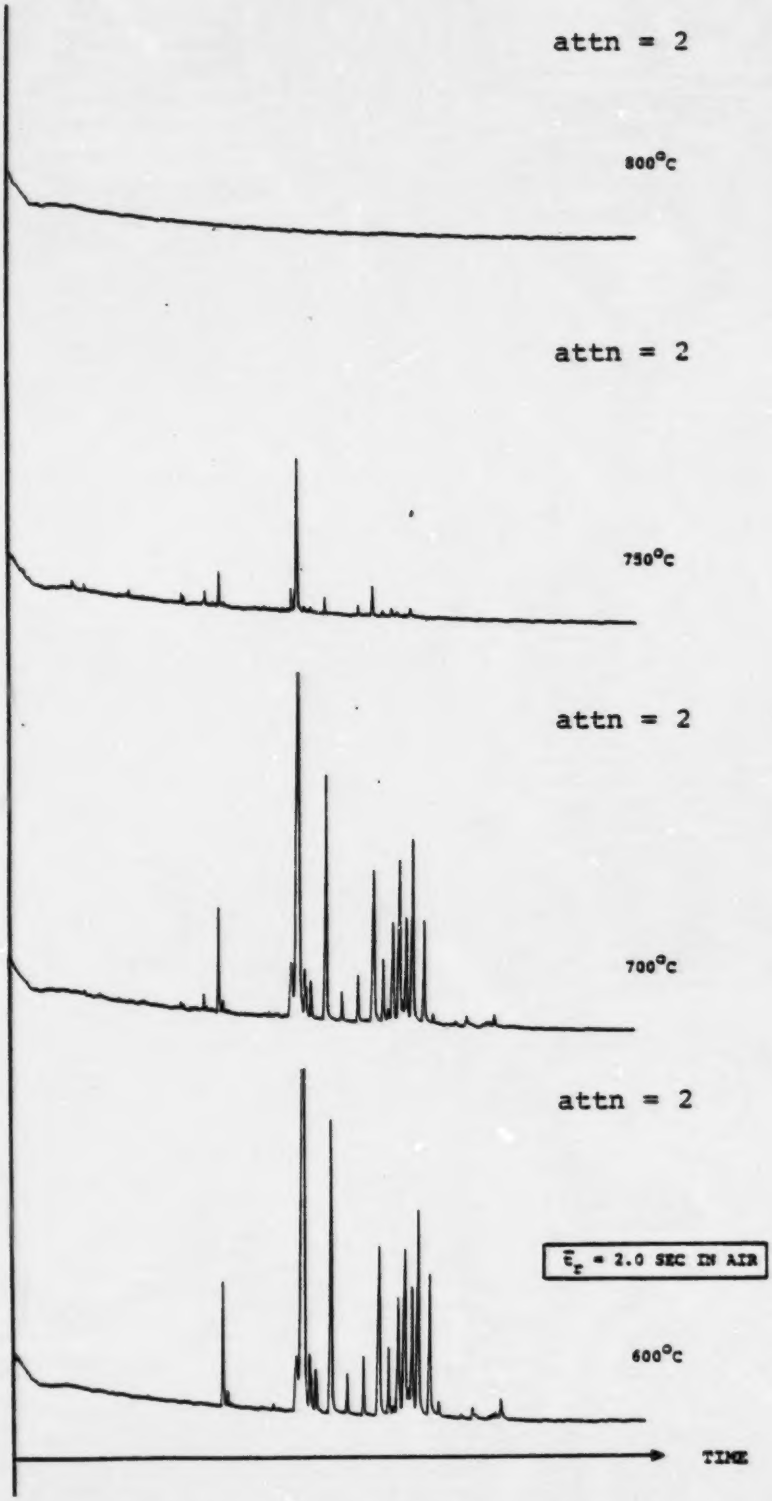


Figure 5.19. Halowax TDAS Tracings.

were subjected to increasing temperatures for 2.0 seconds mean residence time in flowing air. Three components of this mixture were selected for designation; the major constituent, a "typical" constituent, and the 1,2,3,4-tetrachloronaphthalene (which was spiked into the sample). Quantitative data were then generated for these three compounds. These data are presented in Table 5.3. Additional data were obtained for the PCNs in flowing gas streams of 100 percent oxygen and 100 percent nitrogen. These data are also included in Table 5.3. All of the data from the table are plotted in Figure 5.20.

5.6.2 Discussion

From the chromatograms illustrating the thermal decomposition characteristics of the PCN sample in flowing air, two important observations can be made. First, the sample is destroyed to levels below the detection limit (approximately 0.01% for this analysis) at 800°C and second, there is virtually no formation of reaction products during the decomposition of this sample. This is in contrast to the halogenated biphenyls previously discussed, which were detected at levels greater than one percent at 800°C and which also formed significant quantities of thermal reaction products during decomposition.

The PCN data listed in Table 5.3 and plotted in Figure 5.20 are highly informative. The thermal decomposition profiles for each of the three selected constituents are closely grouped with the position of the groups highly dependent upon the oxygen content of the reaction atmosphere. This clearly indicates that this compound is amenable to and dependent upon reaction with oxygen or oxygen containing species for decomposition to occur below 850°C at 2.0 seconds mean residence time. The pathway may be electrophilic radical addition, which is impeded by chlorination, or hydrogen abstraction by an oxygen containing species, a process favored by chlorination. In either event, the intermediate could be stabilized by the planar two centered aromatic structure.

Table 5.3

PCN THERMAL DECOMPOSITION DATA

Thermal Exposure (°C) in Flowing O_2	Weight Percent Remaining		
	Halowax 1001		
	Major Constituent	Typical Constituent	1,2,3,4-Tetrachloronaphthalene
500	100.0	100.0	100.0
600	87.5	80.0	68.0
700	40.0	22.0	7.3
725	4.6	2.0	BDL*
750	0.5	BDL	BDL

Thermal Exposure (°C) in Flowing Air	Weight Percent Remaining		
	Halowax 1001		
	Major Constituent	Typical Constituent	1,2,3,4-Tetrachloronaphthalene
500	100.0	100.0	100.0
600	---	100.0	100.0
700	---	89.5	96.0
750	27.8	18.0	3.6
800	0.5	BDL	BDL

Thermal Exposure (°C) in Flowing N_2	Weight Percent Remaining		
	Halowax 1001		
	Major Constituent	Typical Constituent	1,2,3,4-Tetrachloronaphthalene
700	100.0	100.0	---
800	92.4	96.6	90.9
900	---	63.4	37.3
950	30.9	22.9	6.4
1000	0.9	0.5	BDL

* Below detection level
--- Off-scale response, not measured.

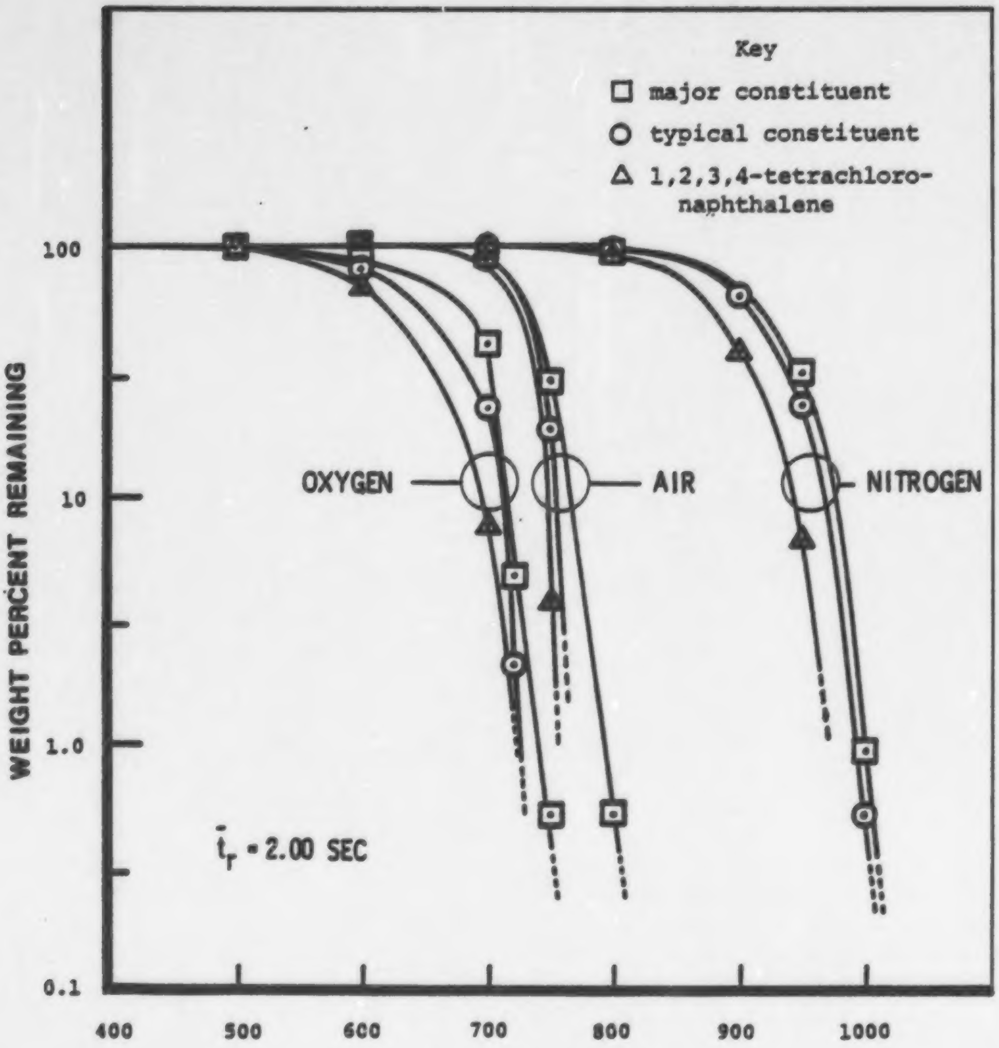


Figure 5.20. PCN Thermal Decomposition Profiles.

This compound is highly stable in the absence of oxygen. Lower energy bimolecular decomposition pathways involving oxygen are excluded and pathways requiring higher temperatures such as unimolecular decomposition increase in importance.

SECTION 6

KINETIC DATA FOR SELECTED COMPOUNDS

The study of reaction kinetics can provide valuable information as to the rates and mechanisms involved in the thermal decomposition of complex molecules. In this section, kinetic methods of data analysis have been utilized to obtain a better understanding of the dynamic processes involved in the thermal decomposition of several compounds and the dependence of these processes on the presence of oxygen in the reaction atmosphere.

6.1 KINETIC STUDIES OF 2,2',4,5,5'-PENTACHLOROBIPHENYL DEGRADATION

The gas phase thermal decomposition kinetics of 2,2',4,5,5'-pentachlorobiphenyl (2,2',4,5,5'-PCB) in flowing air was studied on the TDAS. The data are sufficient to determine the pseudo first-order rate constants for the decomposition and to calculate kinetic parameters that can be incorporated into complex incineration engineering analyses.

6.1.1 Results

The kinetic data of 2,2',4,5,5'-PCB were obtained by measuring the percent of the isomer remaining as a function of residence time at different reactor temperatures.[12] A series of tests were conducted in flowing air at temperatures over the range 650°C to 750°C at 25°C intervals. The effects of temperature and residence time upon the decomposition of this PCB isomer were studied. The experimental conditions are summarized in Table 6.1.

The experimental results are contained in Table 6.2 and a plot of the data is presented in Figure 6.1.

6.1.2 Discussion

The data analysis scheme used for 2,2',4,5,5'-PCB is similar to that already developed for a study of thermal decomposition kinetics of 20 hazardous organic compounds.

TABLE 6.1

EXPERIMENTAL PARAMETERS FOR THE KINETIC ANALYSIS OF THE 2,2',4,5,5'-PENTACHLOROBIPHENYL ISOMER

Reactor Temperature (°C)	Reactor Temperature (°K)	Residence Time (seconds)
650	923	1.0, 2.0, 3.0, 4.0, 4.5
676	949	2.0, 3.0, 4.0, 4.5, 4.8
701	974	2.0, 3.0, 3.5, 4.0, 4.5
726	999	0.5, 1.0, 2.0, 3.0
751	1024	0.5, 1.0, 1.24, 1.5, 2.0

TABLE 6.2

EXPERIMENTAL DATA FOR THE THERMAL DECOMPOSITION OF 2,2',4,5,5'-PENTACHLOROBIPHENYL IN WEIGHT PERCENT OF SAMPLE REMAINING

Mean Residence Time $\bar{t}_r$ (s)	Exposure Temperature T (°C)				
	652	676	700	726	751
0.50	---	---	---	69,79	54
1.00	96	---	---	59,52	39
1.24	---	---	---	---	22
1.50	---	---	---	---	11
2.00	85	79,89	67	27,23	4
3.00	87,82	80	55, 55	10,9	---
3.50	---	---	39	---	---
4.00	80,78	63,62	42,34	---	---
4.50	81	65	26	---	---
4.80	---	65	---	---	---

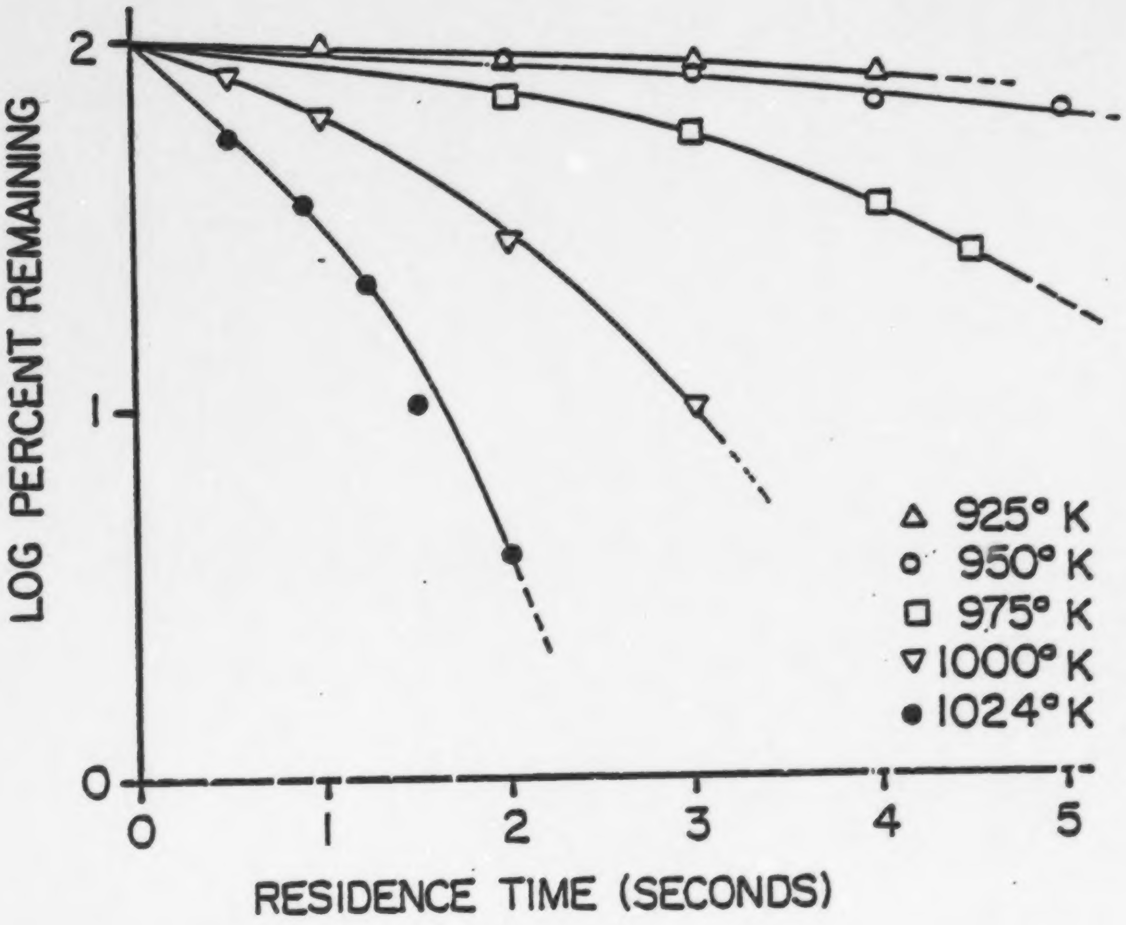


Figure 6.1. The log percent of PCB isomer remaining as a function of residence time and temperature.

We will present a brief overview of the theory; a more detailed discussion has been included in a previous report.[8]

These data were first examined to determine the order dependency of the thermal decomposition of this PCB isomer in the presence of excess oxygen.

$$\mathrm{PCB} + \mathrm{O_2} \xrightarrow{\text{heat}} \text{Products}$$

The kinetics of the reaction can be determined by monitoring the change in concentration of the PCB isomer or a reaction product with time. The reaction velocity can be expressed as:

$$\frac{-d[\mathrm{PCB}]}{dt} = k[\mathrm{PCB}]^a\ [\mathrm{O_2}]^b \qquad (1)$$

Since these studies were conducted in an excess oxygen environment (1000:1 mole ratio), the reaction will appear as a pseudo-a^{th} order. Therefore,

$$\frac{-d[\mathrm{PCB}]}{dt} = k'\ [\mathrm{PCB}]^a \qquad (2)$$

The integrated form of Equation 2 assuming first-order dependence ($a = 1$) for the PCB isomer equals

$$\ell n\ \frac{[\mathrm{PCB}]_t}{[\mathrm{PCB}]_o} = \ell n\ f_r = k't \qquad (3)$$

The data (residence time and percent isomer remaining) best fit the integrated first-order rate expression; that is, a graph of $\ell n\ f_r$ vs. t is approximately linear with a slope of $-k'$.

Using this equation and the data plotted in Figure 6.1, it is then possible to calculate the pseudo-first-order rate constant, k'. The results of these calculations are presented in Table 6.3.

TABLE 6.3

LINEAR REGRESSION VALUES FOR THE PSEUDO-FIRST ORDER RATE CONSTANT, k', FOR THE THERMAL DECOMPOSITION OF 2,2',4,5,5'-PENTACHLOROBIPHENYL

Temperature (°K)	$k'(s^{-1})$	r^2
925	0.051	0.81
949	0.112	0.80
974	0.265	0.88
999	0.827	0.99
1024	1.826	0.95

There is clearly a negative curvature in the plot of log percent remaining versus residence time at higher temperatures. This is the result of a deviation from pure first order kinetics, the negative curvature being an indication that the reaction order is actually slightly less than one at these temperatures. The data do not permit calculation of the exact fractional reaction order, but it is interesting to note that the apparent fractional reaction order of less than one is in opposition to previously observed trends.[8] In the majority of cases, reaction orders were approximately one or slightly greater. Although the deviation from first order kinetics appears small, it would imply that slightly greater destruction efficiencies would be achieved by reducing the concentration of the 2,2',4,5,5'-PCB.

The temperature dependence of the reaction rate constant is given by the Arrhenius equation:

$$k' = A \exp(-E_a/RT) \qquad (4)$$

where:

E_a = the activation energy for the process, kcal $mole^{-1}$

A = the Arrhenius coefficient, s^{-1}

R = the universal gas constant, 1.99 cal $mole^{-1}$ $°K^{-1}$

A plot of $\ell n\ k'$ vs. 1/T will yield the kinetic parameters E_a and A from the slope and intercept, respectively.

The Arrhenius plot for 2,2',4,5,5'-PCB is shown in Figure 6.2. From linear regression analysis of the data, the calculated values for E_a and A are 70 kcal mole^{-1} and 1.3×10^{15} s^{-1}, respectively.

From Equations 3 and 4, one can derive the expression:

$$T_{DE} = 503\ E_a\ [\ell n\ (\frac{-\bar{t}_r A}{\ell n\ f_r})]^{-1} \qquad (5)$$

where:

T_{DE} = temperature required for a given DE in °K
and the other variables are previously defined.

Application of this equation yields a calculated T_{99} of 1,022°K (749°C) and $T_{99.99}$ of 1,051°K (779°C) at $\bar{t}_r$ = 2.0s in flowing air.

The calculated thermal stability is similar to, but slightly less than, that of other partially chlorinated aromatics (i.e., 1,2-dichlorobenzene and 1,2,4-trichlorobenzene). Based on extrapolation of the data to T_{99} or $T_{99.99}$, it would appear to be slightly more stable than 1,2-dichlorobenzene and 1,2,4-trichlorobenzene. For comparison, Table 6.4 presents the data for 2,2',4,5,5'-pentachlorobiphenyl along with the kinetic data for 20 other compounds which have been previously reported. Based on calculated T_{99}, we would classify this compound as moderately stable. The important point is that by any of these measures (calculated or extrapolated T_{99} or $T_{99.99}$), it does not represent an unusually stable species and does not appear to exceed the thermal stability of some other commonplace compounds which we have tested.

We currently feel that electrophilic addition to the aromatic ring structure is the dominant destruction mechanism for aromatics.[8] All of the bond energies in 2,2',4,5,5'-PCB would appear to be greater than 90 kcal/mole. Thus, we would not expect any low energy fragmentation pathways to be available. Thus, we again feel electrophilic addition is the dominant destruction mechanism. This would imply that the thermal stability of this PCB isomer would be similar to that of di- or trichlorobenzene which is, in fact, the observation.

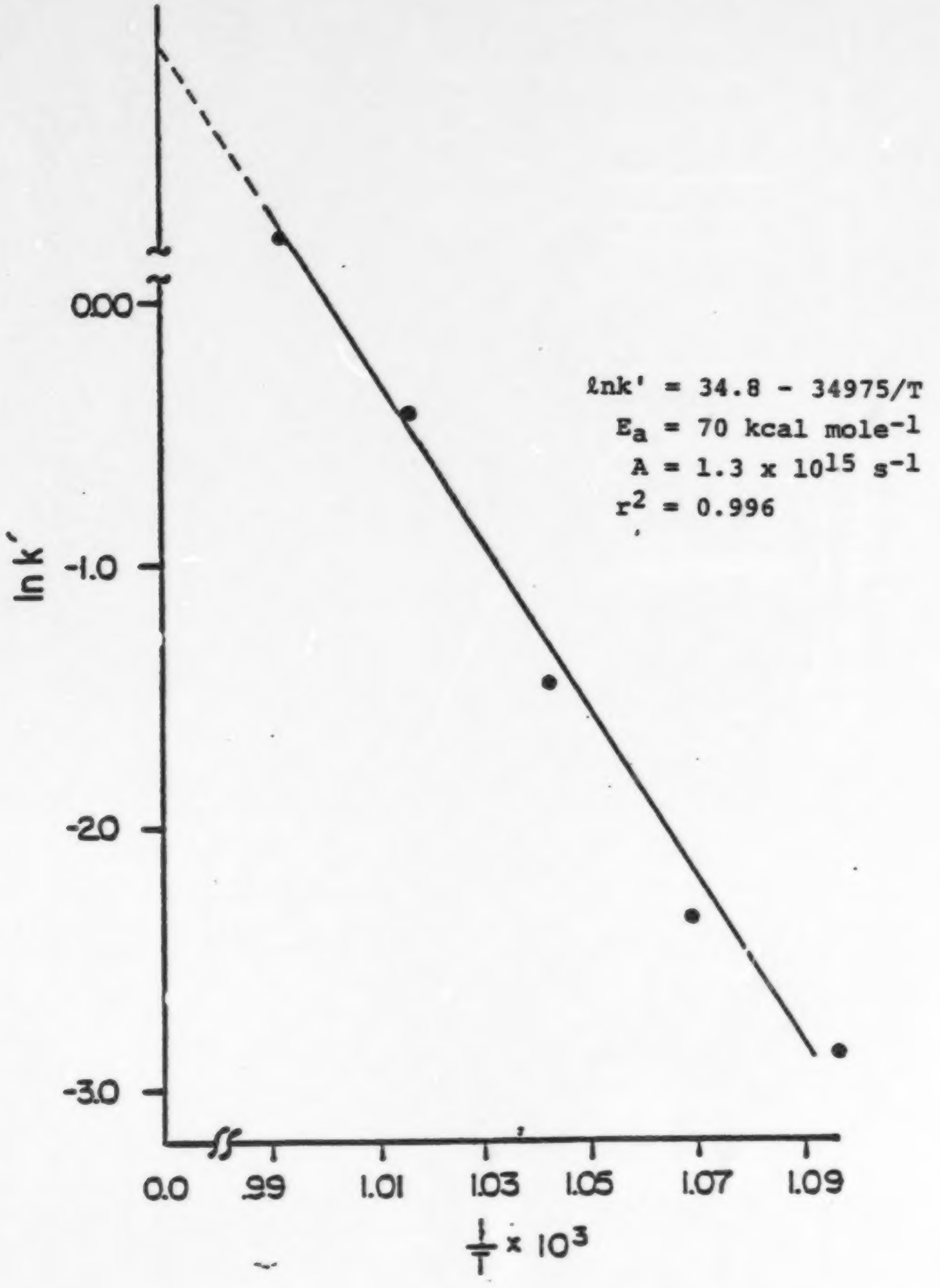


Figure 6.2. Arrhenius Plot for the Thermal Decomposition of 2,2',4,5,5'-Pentachlorobiphenyl.

TABLE 6.4

SUMMARY OF FIRST ORDER KINETIC RESULTS

Compound	A(s^{-1})	E_a(kcal/mole)	Temperature Range	Calculated T_{99}(2) (°C)
Acrylonitrile	1.3×10^6	31	750-810	910
Acetonitrile	4.7×10^7	40	800-850	908
Tetrachloroethylene	2.6×10^6	33	725-825	900
Methane	3.5×10^9	48	700-800	874
Hexachlorobenzene	2.5×10^8	41	710-785	845
1,2,3,4-Tetrachlorobenzene	1.9×10^6	30	700-765	834
Ethane	1.3×10^5	24	675-725	830
Carbon Tetrachloride	2.8×10^5	26	680-730	824
Monochlorobenzene	8.0×10^4	23	600-670	810
Dichloromethane	3.0×10^{13}	64	700-755	796
1,2,4-Trichlorobenzene	2.2×10^8	39	675-725	789
Pyridine	1.1×10^5	24	700-750	767
1,2-Dichlorobenzene	3.0×10^8	39	685-725	766
Hexachlorobutadiene	6.3×10^{12}	59	685-715	763
Benzene	2.8×10^8	38	685-720	757
2,2',4,5,5'-Pentachlorobiphenyl	1.3×10^{15}	70	650-750	749
Aniline	9.3×10^{15}	71	650-700	726
Nitrobenzene	1.4×10^{15}	64	600-650	672
Hexachloroethane	1.9×10^7	29	500-600	641
Chloroform	2.9×10^{12}	49	520-585	606
1,1,1-Trichloroethane	1.9×10^8	32	475-550	601

6.2 OXYGEN DEPENDENCE OF 2,2'4,5,5'-PENTACHLOROBIPHENYL

Thermal decomposition data for 2,2',4,5,5'-Pentachlorobiphenyl (2,2',4,5,5'-PCB) in flowing gas streams with a variety of oxygen concentrations have been obtained. From these data a reaction order with respect to oxygen for the decomposition of 2,2',4,5,5'-PCB has been determined.

6.2.1 Results

Thermal decomposition experiments were conducted using a variety of gaseous atmospheres including 40 percent oxygen in nitrogen, compressed air, 2.5 percent oxygen in nitrogen, and nitrogen. The profiles resulting from these experiments are shown in Figure 6.3. Data obtained during generation of the thermal decomposition profiles enabled calculation of the reaction order with respect to oxygen for 2,2',4,5,5'-PCB at 2.0 seconds residence time. The plot from which this reaction order was derived is included as Figure 6.4.

6.2.2 Discussion

The concentration of oxygen in the reaction atmosphere has a dramatic effect on the thermal stability of 2,2',4,5,5'-PCB. In air (approximately 21 percent oxygen), the temperature for 99.99 percent destruction is about 760°C. In nitrogen with a trace level of oxygen (approximately 100 ppm), this temperature appears to exceed 1,000°C.

A reaction order with respect to oxygen for the decomposition of 2,2',4,5,5'-PCB may be determined. Equation 1, presented in 6.1.2

$$\frac{-d[PCB]}{dt} = k[PCB]^a[O_2]^b \qquad (1)$$

expresses the reaction velocity for the decomposition. Assuming the oxygen concentration is in great excess and setting (a) equal to one (a valid approximation for this compound based on 6.1.2), integration of the velocity expression leads to the equation

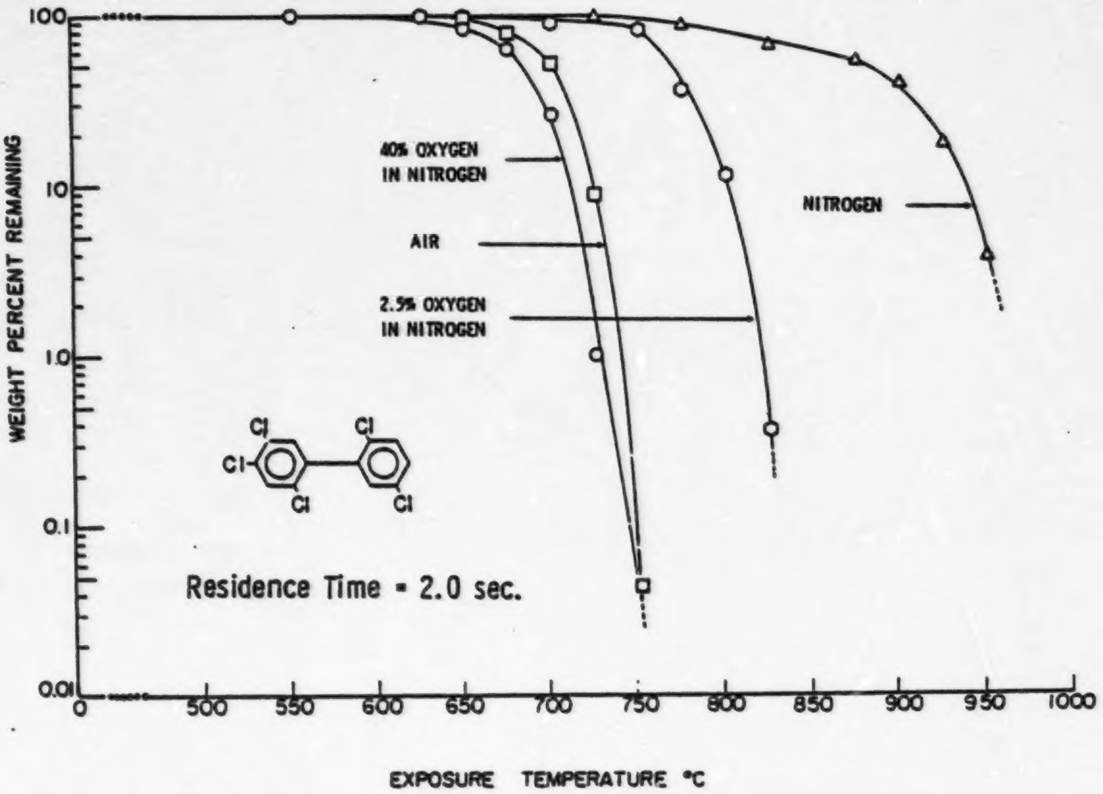


Figure 6.3. Thermal Decomposition Profiles for 2,2',4,5,5'-Pentachlorobiphenyl in Various Oxygen Concentrations.

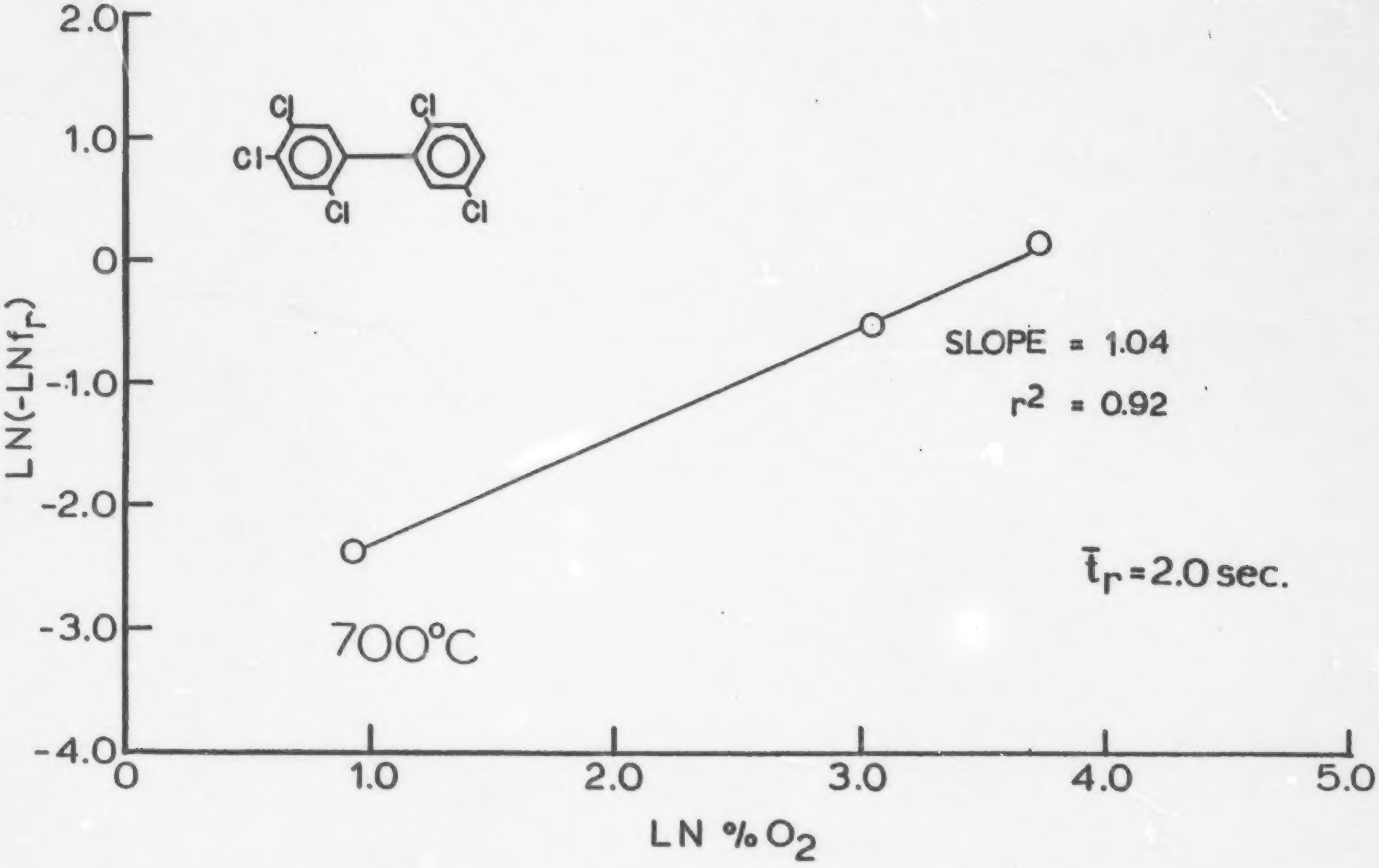


Figure 6.4. Plot of $\ell n(-\ell n f_r)$ vs. ℓn %O_2 for 2,2',4,5,5'-Pentachlorobiphenyl at 700°C.

$$\frac{[\mathrm{PCB}]_t}{[\mathrm{PCB}]_o} = \exp\left(-k[O_2]^b t\right) \qquad (6)$$

Rearranging and letting $\frac{[\mathrm{PCB}]_t}{[\mathrm{PCB}]_o}$ equal the fraction of PCB remaining (f_r) yields the expression:

$$\ell n\,(-\ell n f_r) = b\ \ell n[O_2] + \ell n\ kt \qquad (7)$$

which yields the reaction order with respect to oxygen (b) as the slope of data plotted as $\ell n(-\ell n f_r)$ vs. $\ell n[O_2]$. Such a plot is shown as Figure 6.4 for three data points obtained at 700°C for 2,2',4,5,5'-PCB. The slope of the line connecting these data is 1.04 with a linear correlation coefficient (r^2) of 0.92. These results indicate that the PCB has a first order dependence on the concentration of oxygen over the range of oxygen concentration studied when undergoing decomposition at 700°C.

6.3 OXYGEN DEPENDENCE OF CHLOROBENZENES

The thermal decomposition characteristics of tetrachlorobenzene, pentachlorobenzene, and hexachlorobenzene are of interest for a variety of reasons. Buser, in 1979, demonstrated the formation of polychlorinated dibenzofurans and polychlorinated dibenzo-p-dioxins from tetrachlorobenzene and pentachlorobenzene. Hexachlorobenzene is commonly present at levels from 10 to 15 percent in industrial waste streams and has been observed in the effluent of both pilot and field-scale incinerators.[13,14,6] For these reasons, the thermal decomposition of 1,2,3,4-tetrachlorobenzene (1,2,3,4-TCBz), pentachlorobenzene (PCBz), and hexachlorobenzene (HCBz), including the oxygen dependence of their decomposition, were investigated using the TDAS.

6.3.1 Results

Thermal decomposition profiles were obtained for HCBz, PCBz, and 1,2,3,4-TCBz in flowing gas streams containing a variety of oxygen concentrations. Profiles for all three compounds were obtained in oxygen and nitrogen mixtures containing 2.5, 10.0, 21.0, and 70.4 percent oxygen and also in 100.0 percent oxygen. In some cases, somewhat incomplete profiles are shown as only the data required for the kinetic analyses were obtained. Data for PCBz in industrial grade compressed air and for 1,2,3,4-TCBz in a 5.0 percent oxygen in nitrogen mixture were also obtained. The thermal decomposition profiles are presented in Figures 6.5 to 6.7. All data were obtained at a mean residence time ($\bar{t}_r$) of 2.0 seconds.

6.3.2 Discussion

In Section 6.2 a kinetic treatment of thermal decomposition data was presented which would allow calculation of reaction order with respect to oxygen for thermal decomposition data obtained in flowing gas streams containing a variety of oxygen concentrations. It was the intent of this work to not only establish the reaction order for the three chlorobenzenes, each with a varying degree of chlorination, but to also examine how temperature affected the reaction order with respect to oxygen.

Utilizing the equation presented in Section 6.2

$$\ln(-\ln f_r) = b \ln[O_2] + \ln kt \tag{7}$$

the data can be plotted as $\ln(-\ln f_r)$ vs. $\ln(\%O_2)$ and the reaction order in oxygen (b) obtained from the slope. As in the case of the biphenyl, the use of this equation is justified based on the large excess of oxygen used in the experiments as well as kinetic data indicating that the destruction of chlorobenzenes are approximately first order with respect to the chlorobenzene.[15]

Starting with PCBz, thermal decomposition profiles were obtained in 2.5, 10.0, and 70.4 percent oxygen in nitrogen mixtures, industrial grade air (approximately 21 percent oxygen)

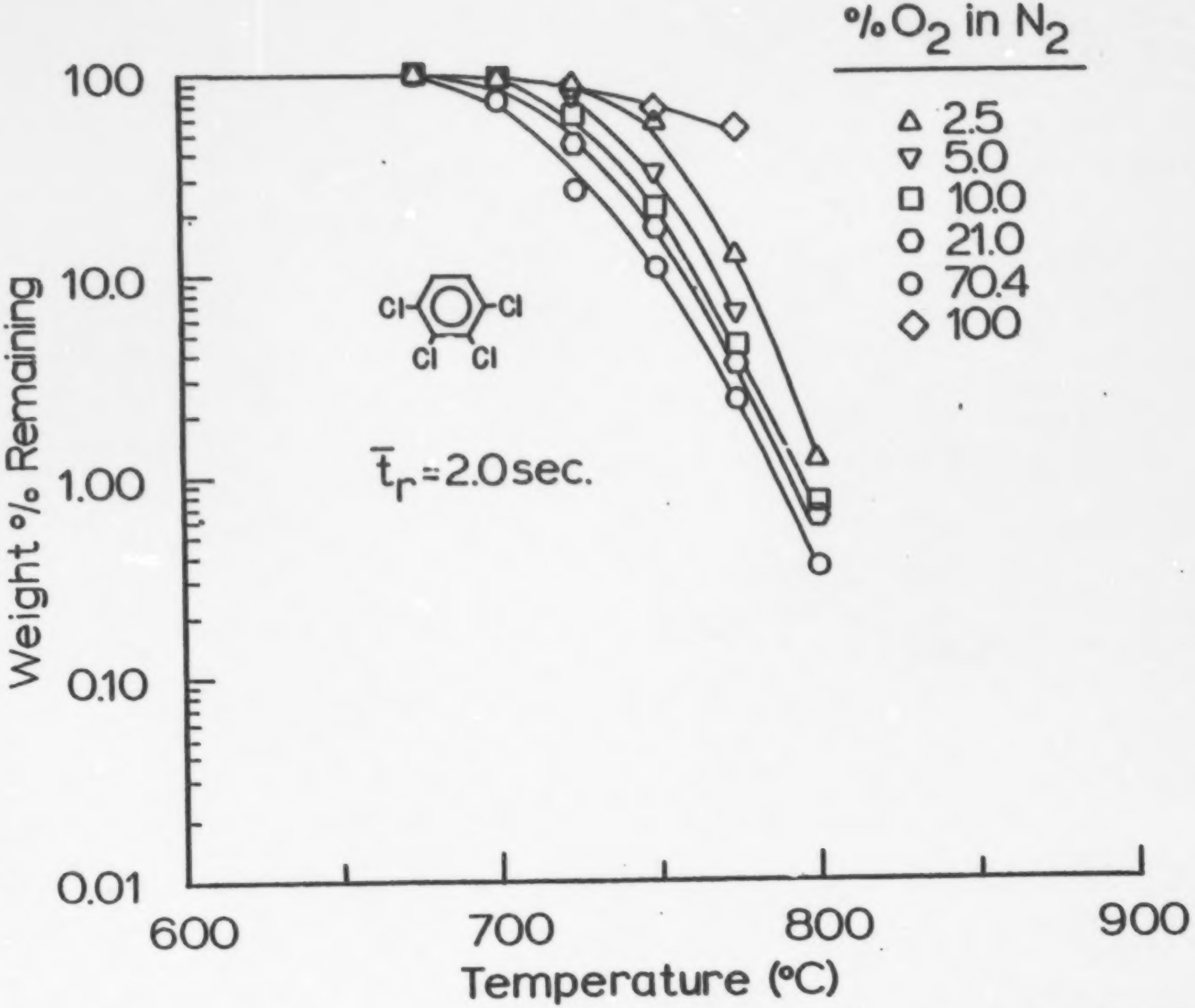


Figure 6.5. Thermal Decomposition Profiles for 1,2,3,4-Tetrachlorobenzene in Various Atmospheres.

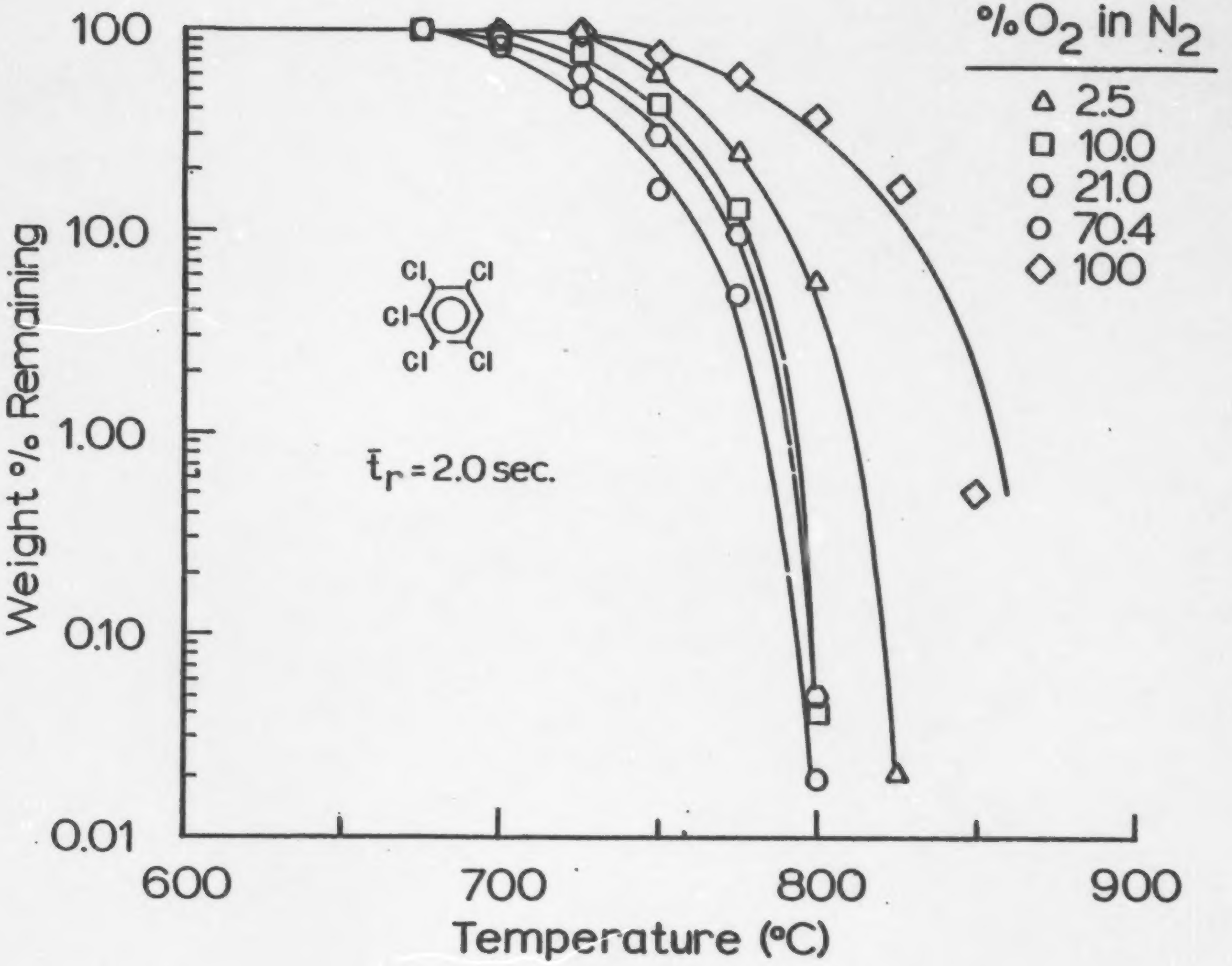


Figure 6.6. Thermal Decomposition Profiles for Pentachlorobenzene in Various Atmospheres.

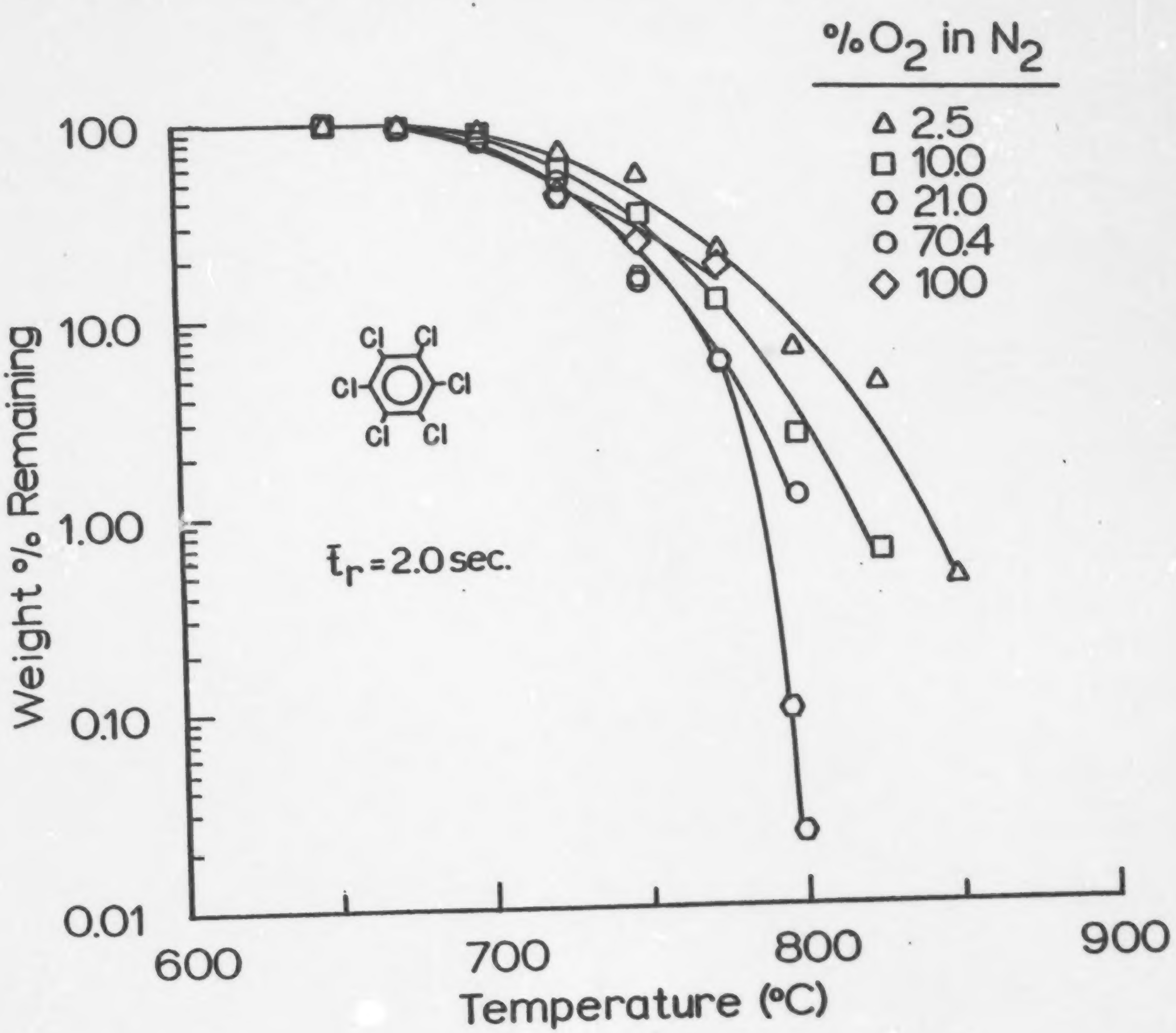


Figure 6.7. Thermal Decomposition Profiles for Hexachlorobenzene in Various Atmospheres.

and 100 percent oxygen.

A good correlation of the data was observed for all oxygen concentrations at and below the 70.4 percent oxygen in nitrogen mixture except for the data obtained in flowing air. Because of this, a cylinder of 21.0 percent oxygen in nitrogen was obtained (from the same supplier as the other mixtures) and a profile obtained in this mixture. A comparison of the thermal decomposition profiles obtained in the industrial grade air vs. that obtained in the specially prepared 21.0 percent oxygen in nitrogen mixture is included in Figure 6.8. Reduction of the data obtained in the oxygen in nitrogen mixture showed a very good correlation with the data for the other mixtures. The plot of $\ell n(-\ell n f_r)$ vs. ℓn (%O_2) for PCBz (Figure 6.9) includes both the compressed air and the 21 percent oxygen in nitrogen data. Only the oxygen in nitrogen mixture data were used in the final data analysis.

The reason for the disparity between the compressed air data and the 21.0 percent oxygen in nitrogen data has not been substantiated, however, it is known that there is a significant difference in the mode of preparation of these gases. The oxygen in nitrogen mixtures are prepared from cryogenic reservoirs and are therefore considered highly pure. The compressed air is pumped from the atmosphere into the high pressure cylinders and may be subject to additional sources of contamination. These contaminants could obstruct a decomposition pathway providing additional thermal stability to certain molecules. Although the data is not presented here, the same type of stabilizing effect was observed for HCBz decomposition in the industrial grade air.

Another interesting effect was observed in these studies. As shown in the $\ell n(-\ell n f_r)$ vs. ℓn(%O_2) plots (Figures 6.9 to 6.11) for the three compounds, a significant negative deviation from linearity occurs as the oxygen content increases beyond a certain point. This indicates that the destruction of the compound at higher oxygen concentrations is lower than what would be expected based on the trend established at the

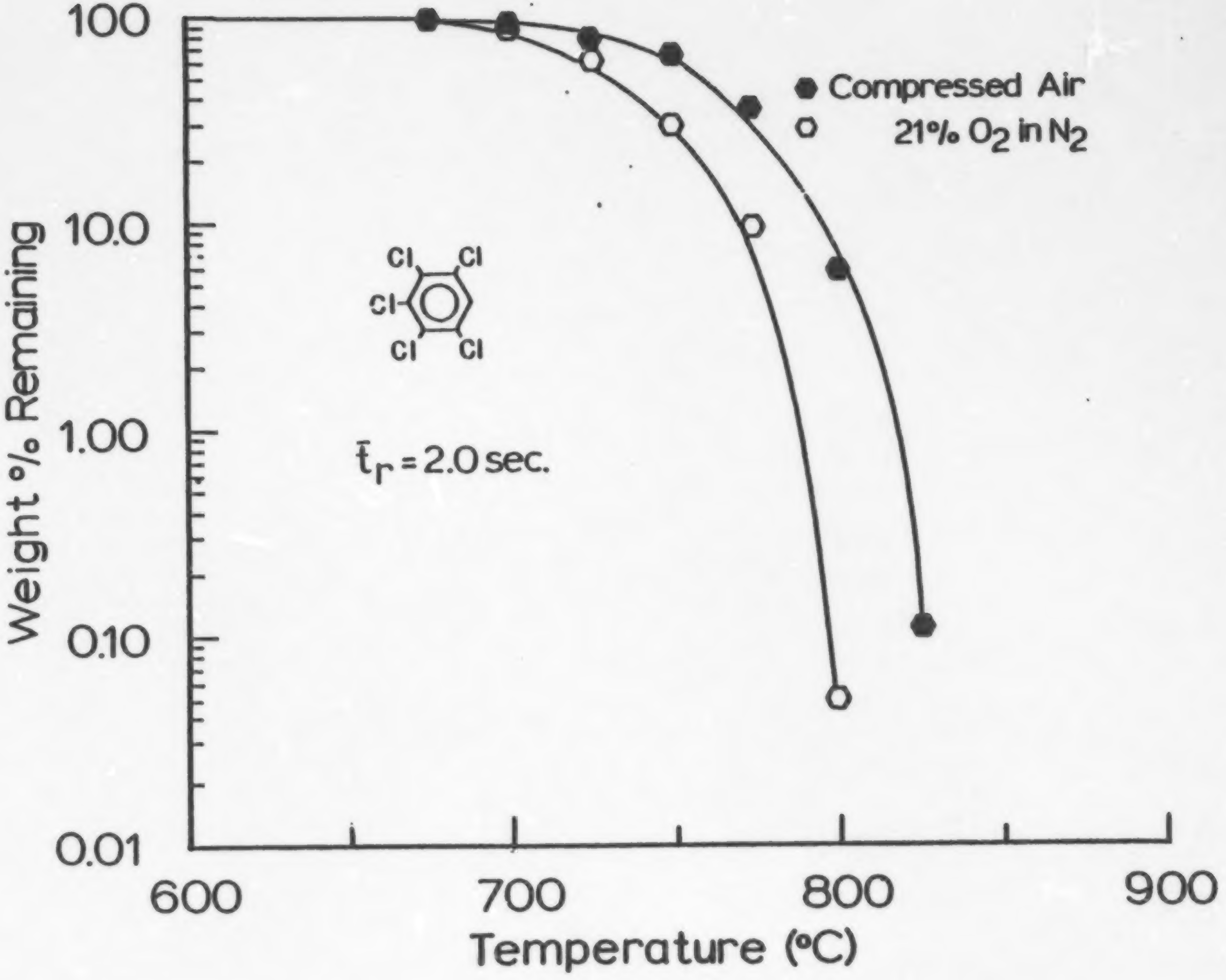
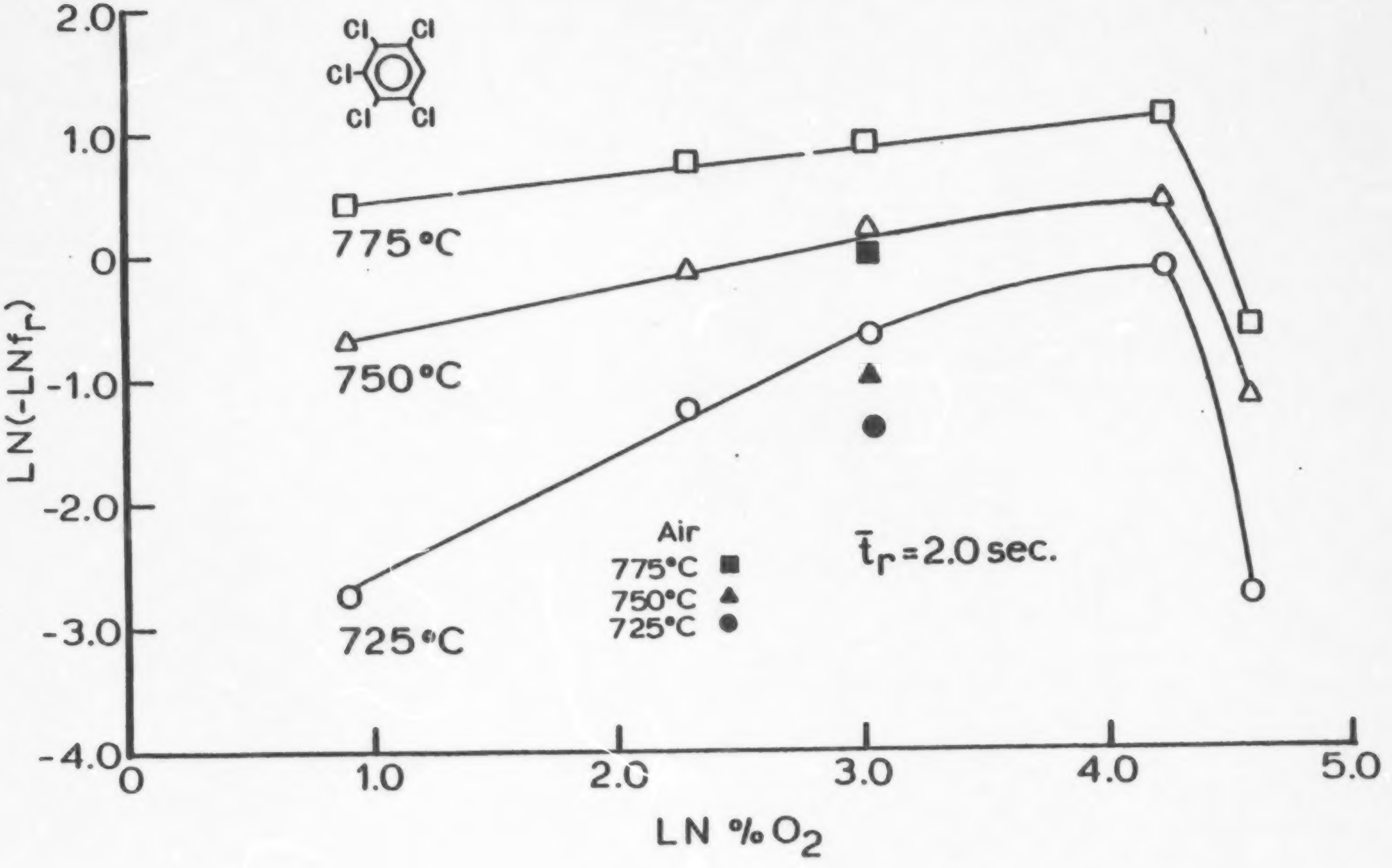


Figure 6.8. Comparison of Thermal Decomposition Profiles for PCBz in Air and in 21% Oxygen/Nitrogen Mixture.



6.9. $\ln(-\ln f_r)$ vs. $\ln \% O_2$ for Pentachlorobenzene.

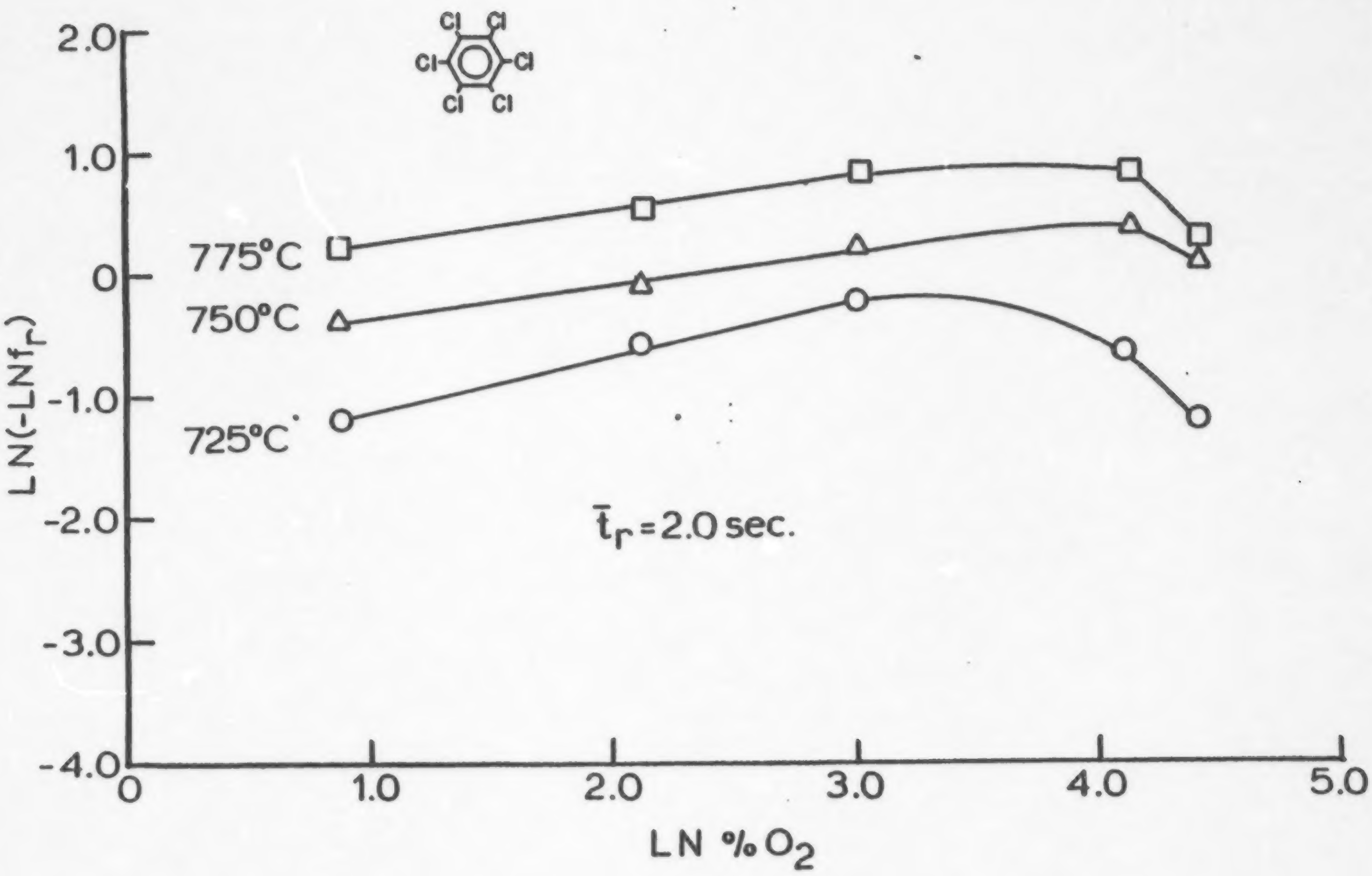


Figure 6.10. $\ell n(-\ell n f_r)$ vs. ℓn %O_2 for Hexachlorobenzene.

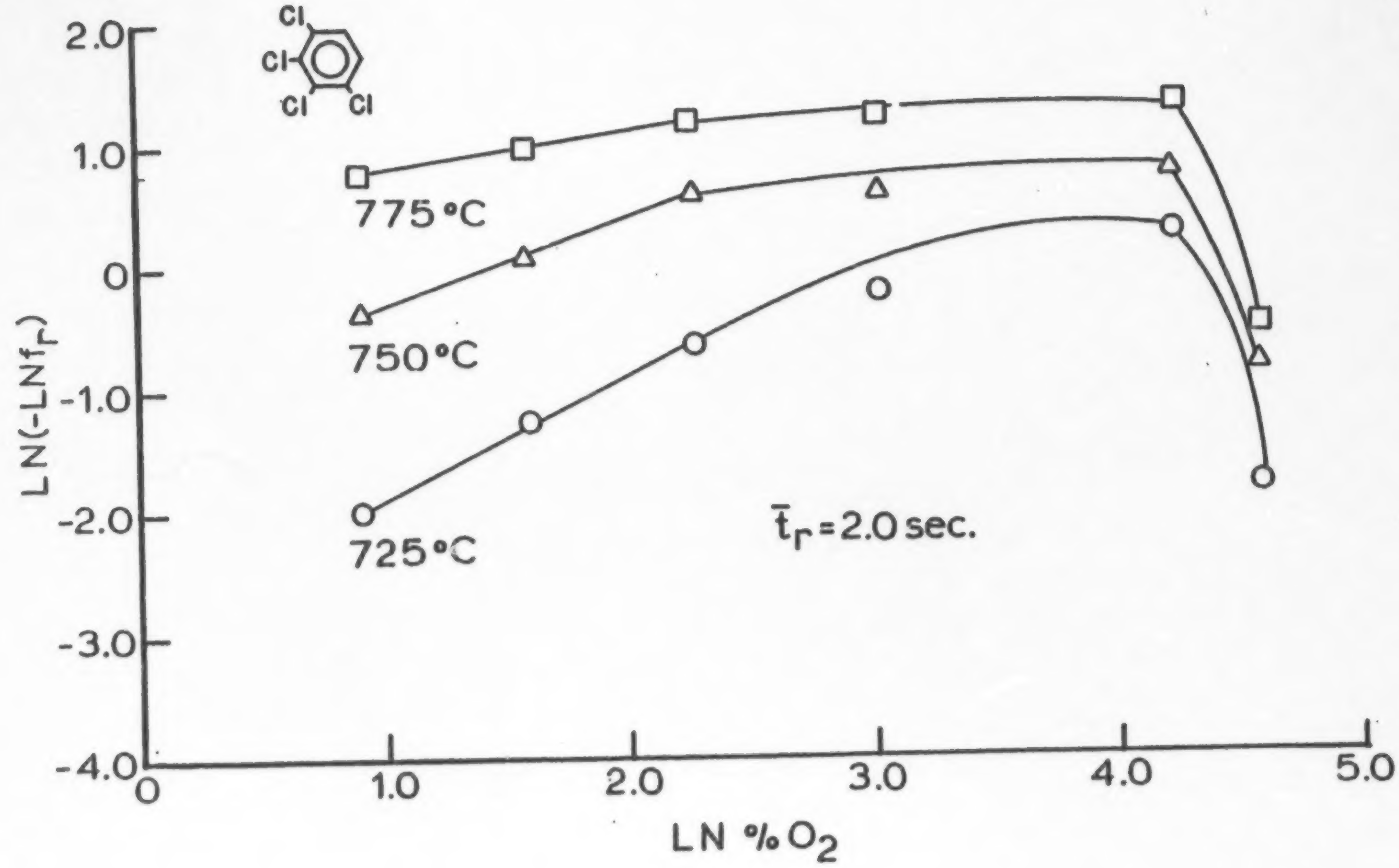


Figure 6.11. $\ln(-\ln f_r)$ vs. $\ln \% O_2$ for 1,2,3,4-Tetrachlorobenzene.

lower oxygen concentrations. In fact, as shown in these plots, the destruction efficiency of 1,2,3,4-TCBz and PCBz was approximately the same or less in 100 percent oxygen than in 2.5 percent oxygen at the temperatures shown. This result was unexpected and would require additional study to be fully explained.

The $\ell n(-\ell n f_r)$ vs. $\ell n(\%O_2)$ plots also show that the deviation from linearity occurs at different oxygen concentrations depending on both the temperature and the compound. As it was desirable to have at least three data points in the linear region and since the deviation occurred at lower oxygen concentrations for 1,2,3,4-TCBz than the other two compounds, an additional data set was obtained for 1,2,3,4-TCBz in a flowing gas stream of 5.0 percent oxygen in nitrogen.

The reaction orders in oxygen for all three compounds were obtained from analyses of the data obtained from the linear region of the curve but did not exceed 21 percent oxygen. These bounds are well justified in that most incineration processes rely on feed air to supply combustion and therefore operate at oxygen concentrations less than 21 percent. The data pertaining to and results of these analyses are included as Tables 6.5-6.7.

Figure 6.12 is a plot of reaction order in oxygen as a function of temperature for 1,2,3,4,-TCBz, PCBz, and HCBz. The dependence on oxygen concentration for the thermal decomposition of 1,2,3,4-TCBz and PCBz at the lower temperatures is higher than the oxygen dependence of HCBz. This may be attributed to a lack of abstractable hydrogen on the HCBz.

Under the specified experimental conditions, the initial decomposition of these compounds could presumably occur by unimolecular decomposition, hydrogen loss by abstraction, or electrophilic attack by a radical. Unimolecular decomposition for these compounds would have activation energies of 80-100 kcal/mole. Alternatively, hydrogen abstraction or electrophilic attack by oxygen containing species would have lower activation energies, in the range of 10 to 50 kcal/mole.

TABLE 6.5

DATA AND RESULTS OF OXYGEN REACTION ORDER DETERMINATION FOR 1,2,3,4-TETRACHLOROBENZENE

1,2,3,4-TETRACHLOROBENZENE

Temp. (°C)	% O_2	LN % O_2	f_r	LN(-LNf_r)	Slope	Intercept	r^2
725	2.5	0.916	0.8734	-1.9998	0.9889	-2.8698	0.992
	5.0	1.609	0.7415	-1.2070			
	10.0	2.303	0.5868	-0.6281			
	21.0	3.045	0.4352	-0.1840			
	70.4	4.254	0.2751	0.2551			
	100.0	4.605	0.8492	-1.8112			
750	2.5	0.916	0.5103	-0.3964	0.7049	-1.0156	0.991
	5.0	1.609	0.3050	0.1718			
	10.0	2.303	0.1672	0.5814			
	21.0	3.045	0.1518	0.6340			
	70.4	4.254	0.1148	0.7722			
	100.0	4.605	0.6504	-0.8436			
775	2.5	0.916	0.1168	0.7642	0.2998	0.5038	0.986
	5.0	1.609	0.0634	1.0146			
	10.0	2.303	0.0386	1.1800			
	21.0	3.045	0.0319	1.2370			
	70.4	4.254	0.0239	1.317[illegible]			
	100.0	4.605	0.5474	-0.5065			

TABLE 6.6

DATA AND RESULTS OF OXYGEN REACTION ORDER DETERMINATION FOR PENTACHLOROBENZENE

PENTACHLOROBENZENE

Temp. (°C)	% O2	LN % O2	f_r	LN(-LNf_r)	Slope	Intercept	r^2
725	2.5	0.916	0.9398	-2.7792	1.0152	-3.6778	0.995
	10.0	2.303	0.7509	-1.2501			
	21.0	3.045	0.5918	-0.6451			
	air	3.045	0.7634	-1.3094			
	70.4	4.254	0.4231	-0.1507			
	100.0	4.605	0.9398	-2.7792			
750	2.5	0.916	0.6057	-0.6904	0.4177	-1.0776	0.999
	10.0	2.303	0.4152	-0.1290			
	21.0	3.045	0.2938	0.2028			
	air	3.045	0.6831	-0.9647			
	70.4	4.254	0.1790	0.5425			
	100.0	4.605	0.7366	-1.1851			
775	2.5	0.916	0.2188	0.4184	0.2115	0.2341	0.989
	10.0	2.303	0.1208	0.7484			
	21.0	3.045	0.0940	0.8605			
	air	3.045	0.3633	0.0124			
	70.4	4.254	0.0497	0.0992			
	100.0	4.605	0.5893	0.6371			

TABLE 6.7

DATA AND RESULTS OF OXYGEN REACTION ORDER DETERMINATION FOR HEXACHLOROBENZENE

HEXACHLOROBENZENE

Temp. (°C)	% O_2	LN % O_2	f_r	LN(-LNf_r)	Slope	Intercept	r^2
725	2.5	0.916	0.7262	-1.1397	0.4717	-1.6056	0.973
	10.0	2.303	0.5827	-0.6160			
	21.0	3.045	0.4068	-0.1060			
	70.4	4.254	0.4717	-0.2858			
	100.0	4.605	0.4114	-0.1186			
750	2.5	0.916	0.4247	-0.1551	0.3149	-0.4876	0.904
	10.0	2.303	0.3270	0.1114			
	21.0	3.045	0.1756	0.5536			
	70.4	4.254	0.1533	0.6288			
	100.0	4.605	0.2649	0.2840			
775	2.5	0.916	0.2148	0.4305	0.2807	0.1640	0.994
	10.0	2.303	0.1120	0.7836			
	21.0	3.045	0.0597	1.0362			
	70.4	4.254	0.0612	1.0273			
	100.0	4.605	0.1966	0.4865			

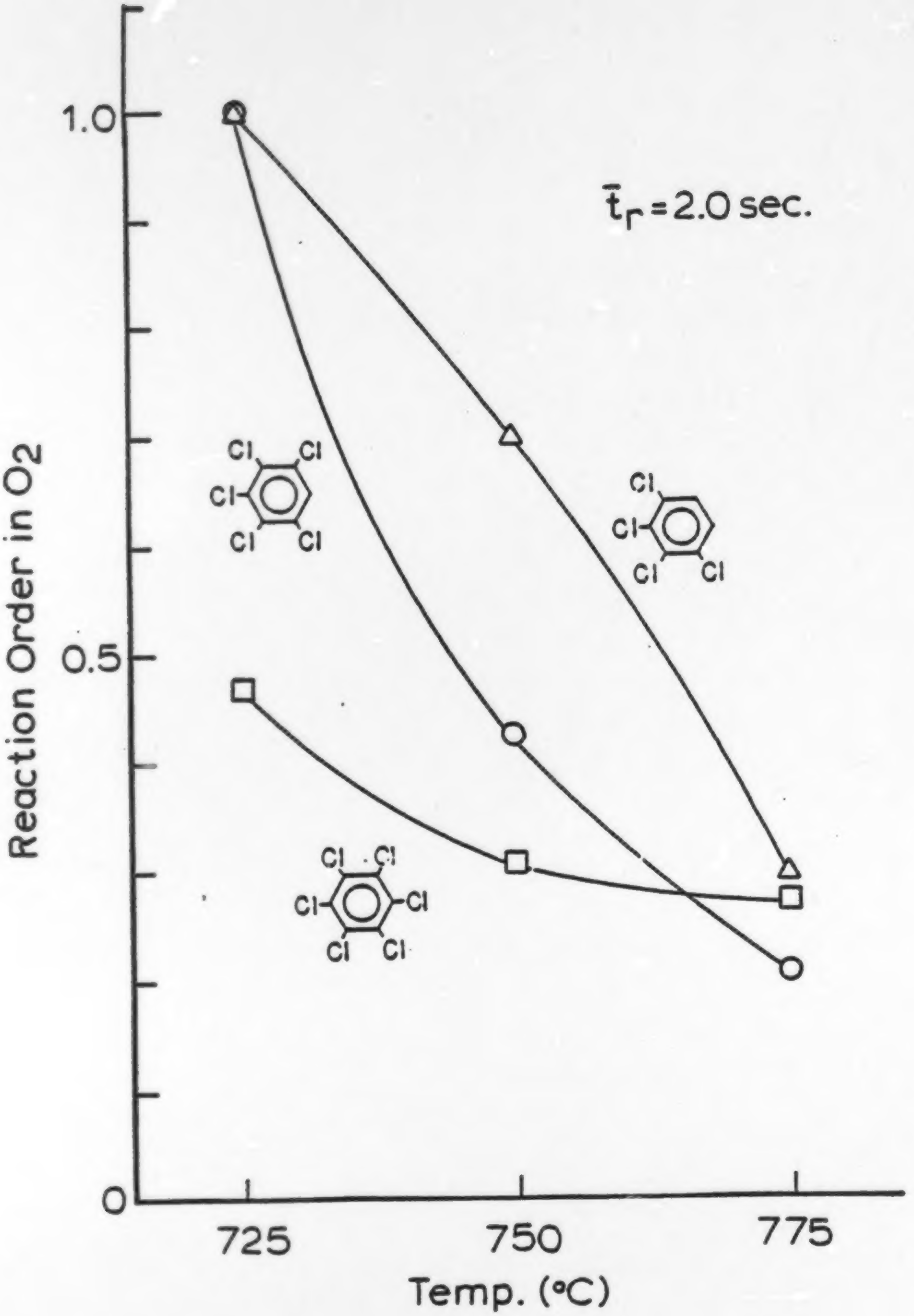


Figure 6.12. Reaction Order in Oxygen vs. Temperature for 1,2,3,4-TCBz, PCBz, and HCBz.

Hexachlorobenzene has no hydrogen for abstraction or participation in the formation of reactive radical species such as the hydroxyl radical. Therefore, decomposition of HCBz is primarily limited to unimolecular pathways and the oxygen dependence is low. As 1,2,3,4-TCBz and PCBz do contain hydrogen, these molecules are amenable to the lower energy bimolecular pathways involving oxygen and therefore, show a higher dependence on oxygen concentration at 725°C and 750°C.

At 775°C, the reaction order curves converge toward a common value. At this temperature sufficient thermal energy is available such that activation energies are no longer controlling and reaction frequency determines the decomposition pathway. Since frequencies for unimolecular decomposition are typically 10^4 to 10^7 times higher than those for oxidative pathways, unimolecular decomposition becomes predominant. The oxygen dependence of 1,2,3,4-TCBz and PCBz is consequently reduced. The residual oxygen dependence at higher temperatures may be due to oxygen associated decomposition of a metastable, intermediate adduct in addition to the more straightforward pathways such as hydrogen abstraction by oxygen or reaction of the chlorobenzenes with radicals.

SECTION 7

MODIFICATIONS OF THE TDAS

Early laboratory studies [5,16] which investigated the thermal destruction of pesticides such as Kepone, Mirex, and DDT clearly showed that it was extremely important to measure and identify both the decomposition behavior of the parent organic substance and the various stable reaction products that were formed during the thermal decomposition process. Consequently, a sophisticated thermal instrumentation system was needed to perform laboratory-scale studies of thermal degradation. The thermal decomposition analytical system (TDAS) was designed [7,17] to fulfill this need. Its construction was completed in 1979. In recent years, with the advent of new materials and new technology, it became evident that several modifications could be made to the TDAS which would enhance its capabilities. A discussion of the rationale for these changes and a description of the modifications follows.

7.1 RATIONALE OF TDAS RECONFIGURATION

Many of the design aspects associated with the TDAS and its performance were described earlier in this report. However, before discussing certain modifications, refinements, and a general reconfiguration of the TDAS, it is instructive to review the original procedure for transporting the sample downstream of the effluent trap.

Figure 7.1 shows a schematic of the flowpath for transporting previously trapped species. It is seen from this figure that a split portion of the sample would normally pass into a high-resolution open tubular column wherein the condensible species would be retained at the inlet region. These retained species (solutes) would then be separated and detected during the subsequent programmed temperature GC analysis.

The vast majority of tests conducted with the TDAS were performed using this mode of effluent transport. However, some

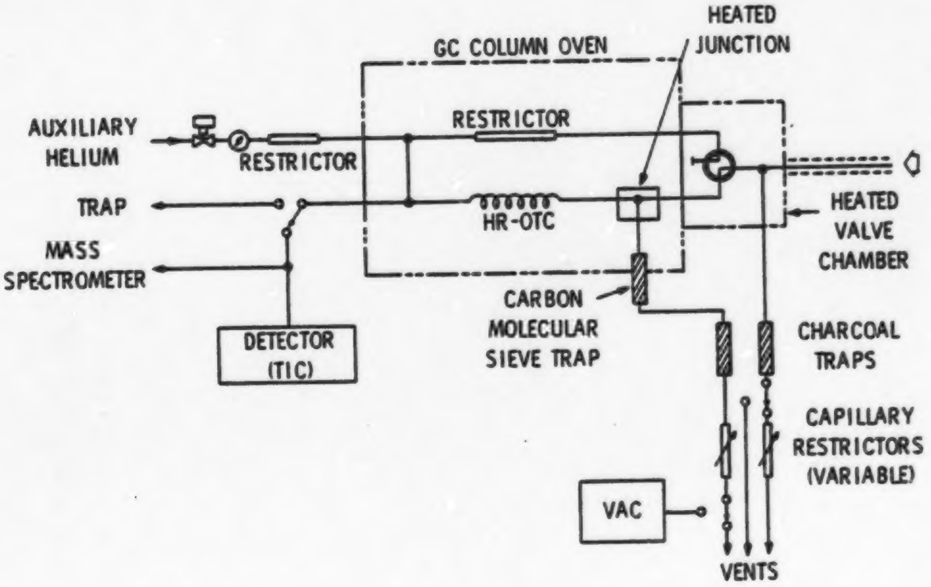

HEATED
JUNCTION
GC COLUMN OVEN
AUXILIARY
HELIUM
RESTRICTOR
RESTRICTOR
TRAP
HR-OTC
HEATED
VALVE
CHAMBER
MASS
SPECTROMETER
CARBON
MOLECULAR
SIEVE TRAP
DETECTOR
(TIC)
CHARCOAL
TRAPS
CAPILLARY
RESTRICTORS
(VARIABLE)
VAC
VENTS

Figure 7.1. Schematic of Gas Transport Downstream of Collection Trap.

tests were conducted whereby the valve (located in the heated valve chamber) was switched to the other position, thus permitting a small fraction of the volatile gaseous species to be transferred to the mass spectrometer where they were continuously monitored. Tests in which certain chlorinated hydrocarbons were thermally decomposed showed considerable quantities of chlorine gas, HCl, CO_2, and water.

The early samples that were subjected to TDAS analysis were complex mixtures which contained low volatility compounds, e.g., molecular weights ranging from 100 to 500 amu. To separate these complex mixtures, high resolution gas chromatographic (HRGC) columns were needed. When using these HRGC columns, the low molecular weight species would not be retained in the chromatographic arrangement shown in Figure 7.1. The chromatographic column oven chamber had a minimum operating temperature of approximately 25°C, and many of the volatile species would migrate through a thin film HRGC column at these temperatures.

As originally equipped, the LKB 2091 GC-MS uses a two-stage stainless steel separator to interface the gas chromatographic column and the ion source inlet of the mass spectrometer. Although this particular separator design was widely used, stainless steel is certainly not as inert a material as glass or quartz. For operation with open tubular columns, a gold-lined transfer tube was provided for transporting the effluent from the GC oven interior and into the inlet region of the two-stage separator.

When high molecular weight substances e.g., greater than 300 amu, were tested using the TDAS, it was observed that considerable solute zone distortion was occurring and adsorption of low level constituents was taking place. Figure 7.2 shows a chromatogram of a mixture of hydrocarbons, chlorinated hydrocarbons, and brominated hydrocarbons which was obtained using a specially prepared open tubular GC column. This particular chromatogram was obtained using a separate gas chromatographic

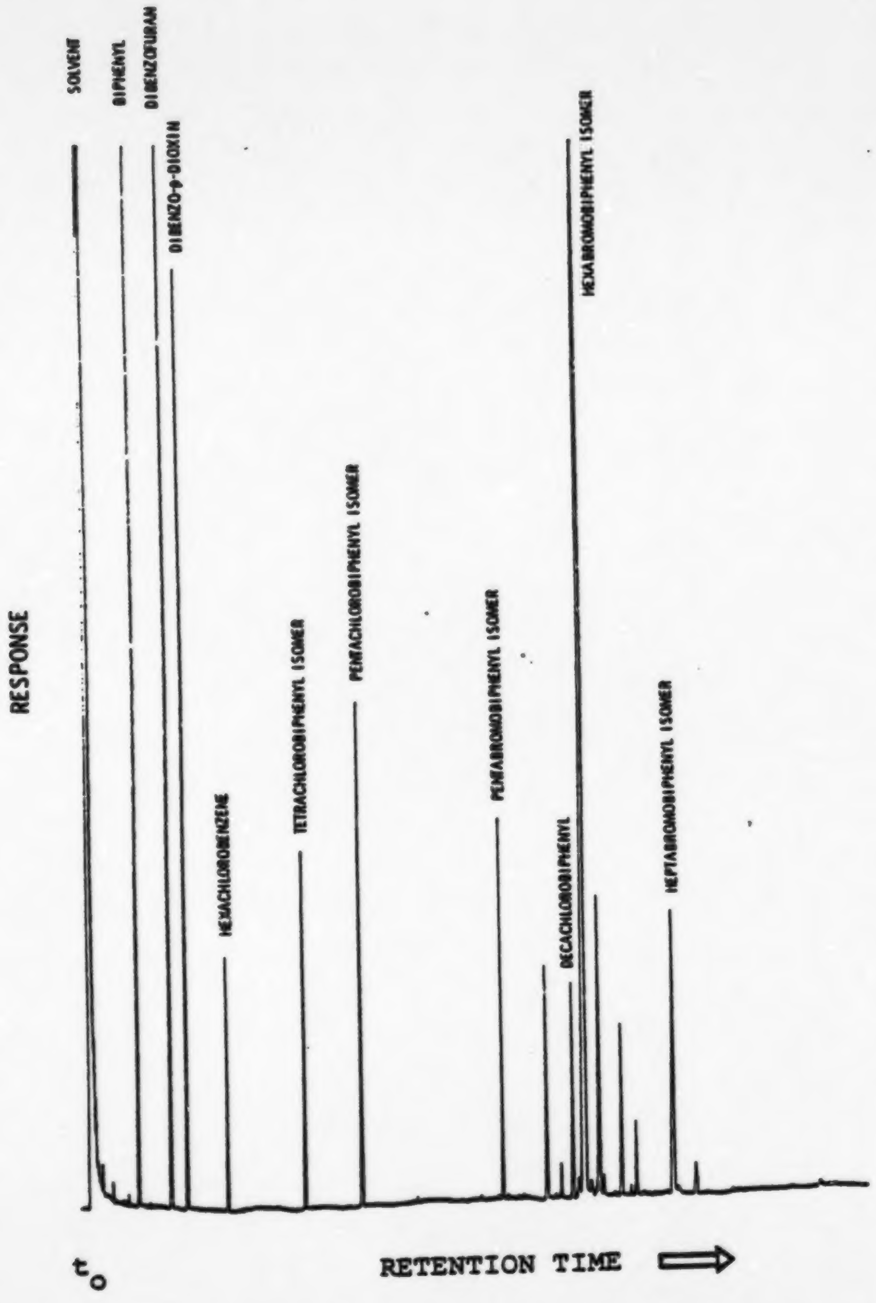
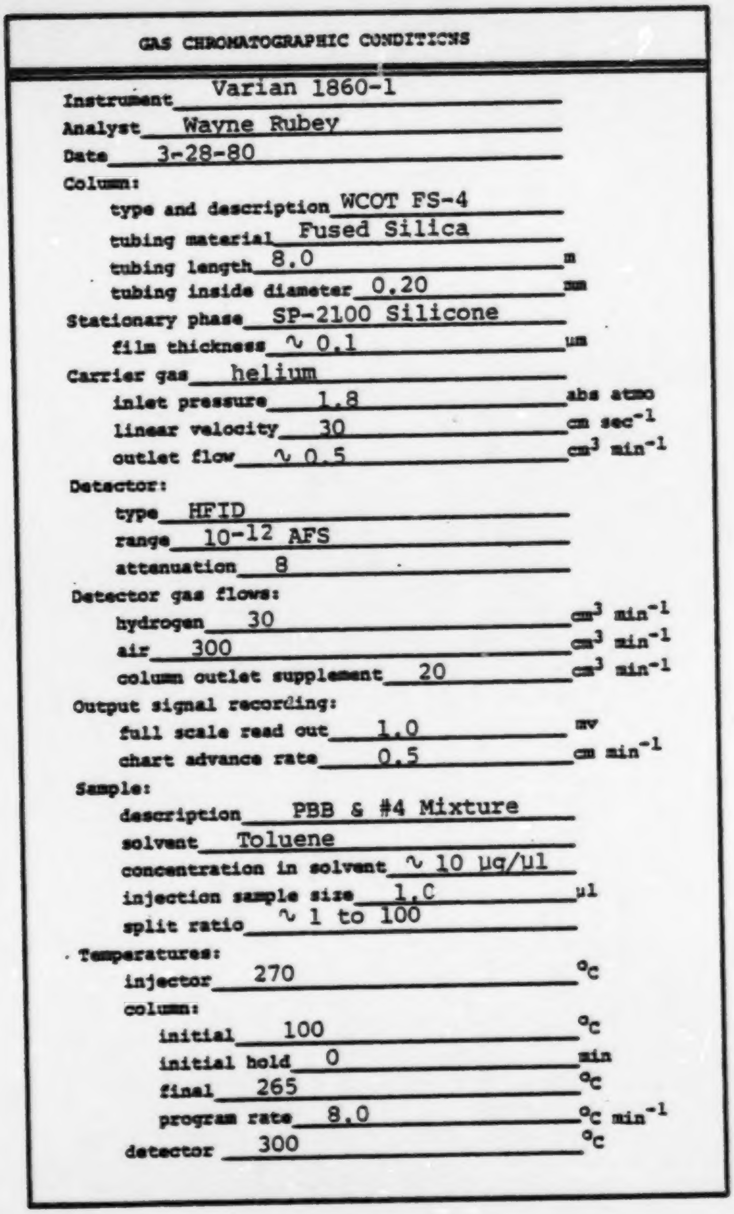


Figure 7.2. Chromatogram of Select Mixture Obtained in Separation Instrument.

instrument (see chromatographic conditions in Figure 7.3). It is seen from Figure 7.2 that the chromatographic behavior of the various solutes is quite acceptable as the recorded emerging solute zones are narrow and symmetrical. However, when this same column was installed into the gas chromatograph of the LKB 2091, severe solute zone distortion was observed as evidenced by the chromatogram shown in Figure 7.4. This adverse transport behavior was especially noticeable for the heavy polybrominated biphenyl compounds. The lower molecular weight solutes were eluted in a somewhat satisfactory manner.

Numerous corrective measures were undertaken to improve this solute transfer. For example, improving the uniform thermal control over the gold-lined transfer tube was undertaken with negligible improvement in subsequent chromatograms. Heating the entire separator oven to higher temperatures showed distinct improvement in solute transport. However, even at separator temperatures of 320°C, significant levels of solute distortion and adsorptivity remained. Even so, this action indicated that the transport problem resided in the two-stage stainless steel separator.

Figure 7.5 is a sectional drawing of the two-stage stainless steel separator that was employed in the LKB 2091 instrument. Further inspection of this intricate multi-component assembly revealed the presence of several unswept recesses, partially covered spanner wrench blind holes, and other cavities which would adversely affect efficient transport of gas-phase species. Also, due to the nature of these unswept recesses, crucial surfaces within the separator were subject to organic contamination and could be easily coated with ferrule degradation products, stationary phase bleed, and other upstream contaminant sources. It was evident that to obtain high-resolution separations involving the heavier organic compounds, it would be necessary to modify or replace the interface between the chromatograph and the mass spectrometer. Also, it was anticipated that



GAS CHROMATOGRAPHIC CONDITIONS

Instrument Varian 1860-1
Analyst Wayne Rubey
Date 3-28-80
Column:
- **type and description** WCOT FS-4
- **tubing material** Fused Silica
- **tubing length** 8.0 m
- **tubing inside diameter** 0.20 mm

Stationary phase SP-2100 Silicone
- **film thickness** ∿ 0.1 um

Carrier gas helium
- **inlet pressure** 1.8 abs atmo
- **linear velocity** 30 cm sec^{-1}
- **outlet flow** ∿ 0.5 cm^3 min^{-1}

Detector:
- **type** HFID
- **range** 10^{-12} AFS
- **attenuation** 8

Detector gas flows:
- **hydrogen** 30 cm^3 min^{-1}
- **air** 300 cm^3 min^{-1}
- **column outlet supplement** 20 cm^3 min^{-1}

Output signal recording:
- **full scale read out** 1.0 mv
- **chart advance rate** 0.5 cm min^{-1}

Sample:
- **description** PBB & #4 Mixture
- **solvent** Toluene
- **concentration in solvent** ∿ 10 μg/μl
- **injection sample size** 1.0 μl
- **split ratio** ∿ 1 to 100

Temperatures:
- **injector** 270 °C
- **column:**
  - **initial** 100 °C
  - **initial hold** 0 min
  - **final** 265 °C
  - **program rate** 8.0 °C min^{-1}
- **detector** 300 °C

Figure 7.3. Conditions for GC Separation.

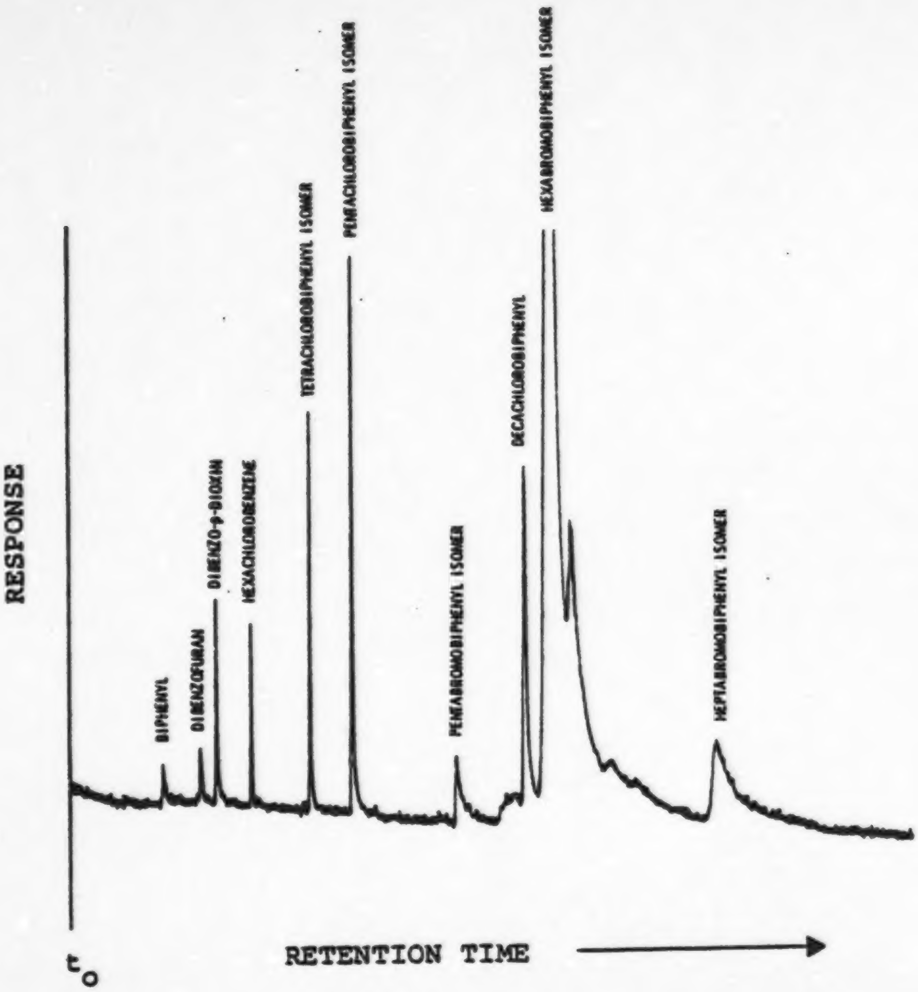


Figure 7.4. Chromatogram of Select Mixture Obtained with TDAS (two-stage stainless steel separator in place).

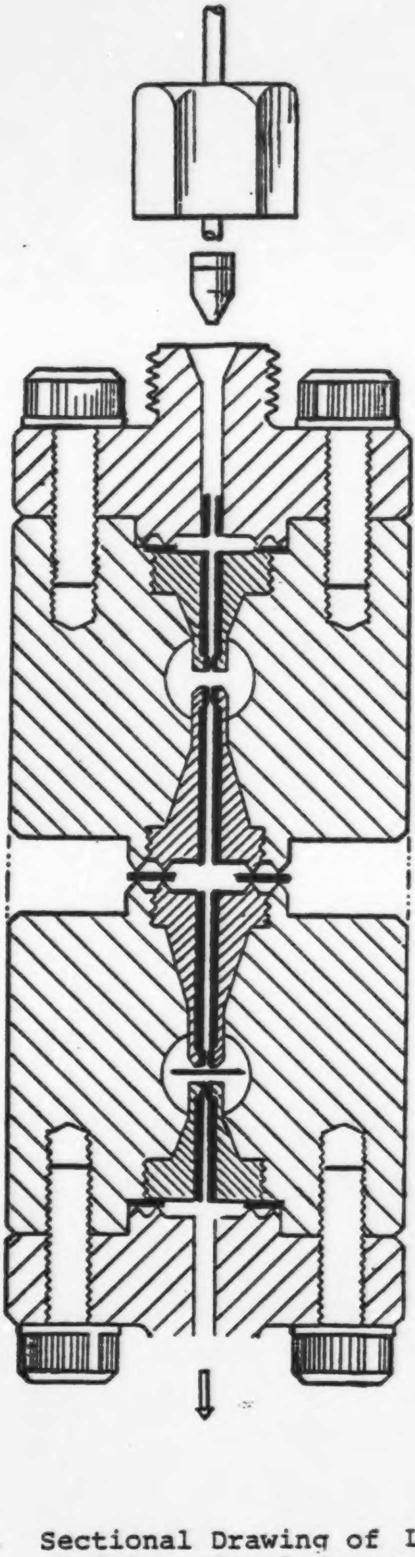


Figure 7.5. Sectional Drawing of LKB Two-Stage Stainless Steel Separator.

a wider range of types of samples would be subjected to thermal decomposition studies using the TDAS.

Several other system modifications were also undertaken. For instance, there was a need to have access to a sample injector on the chromatograph so that for certain applications, the column could be disconnected from the TDU exit and attached to an insertion port. Samples could then be admitted to the chromatograph and immediately passed into the mass spectrometer. This would permit conventional GC-MS analyses to be conducted and provide a more rapid means of calibrating both the gas chromatograph response and the mass spectrometer. This was not an easy task to perform when the open tubular columns were of the non-flexible glass variety such as Pyrex or alkali glass construction. However, this was now possible with the new flexible open tubular columns.

There was also a need for expanding the capabilities of the mass spectrometer and associated computer software so that multiple ion detection (MID) could be performed. This modification to the TDAS would permit both increased sensitivity and selective detection of certain solutes which would elute in the presence of other emerging solute zones. There was a need for thermally testing extremely toxic compounds and to perform these types of studies, it would be necessary to have a protective enclosure surrounding the sample insertion portion of the TDAS. In some experiments, it was desirable to obtain analytical information on compounds that were only present at trace level concentrations. Therefore, it would be necessary to remove any residual adsorptive sites and transition regions from the gas transport flowpath of the TDAS.

A considerable amount of work could be conducted with the TDAS without sending the effluent to the mass spectrometer. For example, if a special detector were appropriately installed in the gas chromatograph and if the column exit could be readily attached to this detector, then many experiments could be conducted in this mode of operation.

7.2 DESCRIPTION OF TDAS MODIFICATIONS, REFINEMENTS, AND RECONFIGURATIONS

Recent technological advances now permit several desirable features to be incorporated into the TDAS. With the advent of flexible fused silica capillary tubing, it is now possible to readily disconnect and reconnect both the entrance and the exit of an open tubular column in a gas chromatographic system. This was not the case with the earlier non-flexible glass capillary columns. Also, inert fused silica tubing now permits improved transport behavior from one point of the system to another.

With the introduction of the new chemically bonded stationary phases and polyimide outer coatings for the fused silica capillary, cryogenic temperature programming has become an extremely valuable procedure for conducting important gas chromatographic separations. In fact, it was, in part, these two technological advances that permitted the feasibility, design, and development of another laboratory system[18] which is capable of rapidly generating gas-phase thermal decomposition data.

The difficulties associated with the stainless steel two-stage separator, however, were not easily addressed and eventually it was decided to abandon this particular interface for several reasons, not the least of which was the poor gas transport properties through the various intricately connected stainless steel components as shown earlier in Figure 7.5. Several other GC-MS interfaces were considered and some were evaluated in the TDAS arrangement. For example, a specially designed open split interface was obtained from J & W Scientific, Inc. as we were informed that this device would be an acceptable interface for our system. However, the existing pumping capacity of the LKB 2091 vacuum system was not sufficient to deal with the 1.0 to 3.0 cm^3 min^{-1} of helium gas that would have to be pumped from the ion source in order to maintain an operating pressure of 1×10^{-6} Torr.

Another evaluation of the revised LKB separator was also conducted wherein only one set of jets was used for separating the carrier from the solutes of interest. This modified single-stage separator (see Figure 7.6) showed improved performance, however, adsorption and the unswept recesses remained as hindrances to quantitative transport of high molecular weight solutes.

A direct connection of the column exit into the ion source was also investigated both with the existing pumps that were on the mass spectrometer and with a much higher capacity pump (Edwards High Vacuum, Inc., part number 63C) that was borrowed for testing purposes. Due to constrictions of the stainless steel vacuum conduit, adequate vacuum levels could not be obtained within the ion source or the analyzer section of the mass spectrometer. Consequently, after consultation with several other mass spectrometer specialists, the final solution was the installation of a Scientific Glass Engineering glass jet separator, part number 113501. A photograph of this type of component is shown in Figure 7.7. The interfacing of this separator to the other mass spectrometer components and gas chromatographic terminations required considerable machining and delicate glass blowing by the respective laboratories at the University. This is a single-stage glass jet separator, and it has been used with many systems which have the same pumping capacity as the vacuum system of the LKB 2091.

The single-stage glass jet separator can accept a range of carrier gas flow rates such as those generated by the newly developed narrow-bore fused silica open tubular columns and those of the wide bore construction. Both of these open tubular columns can be obtained with a thick film of chemically bonded phase. These particular columns provide considerably expanded capacities for samples having solutes with ten times the normal concentration.

Cryogenic programmed temperature gas chromatography was needed for the reconfigured TDAS. It was therefore necessary to abandon the Pye 104 gas chromatograph which was an integral

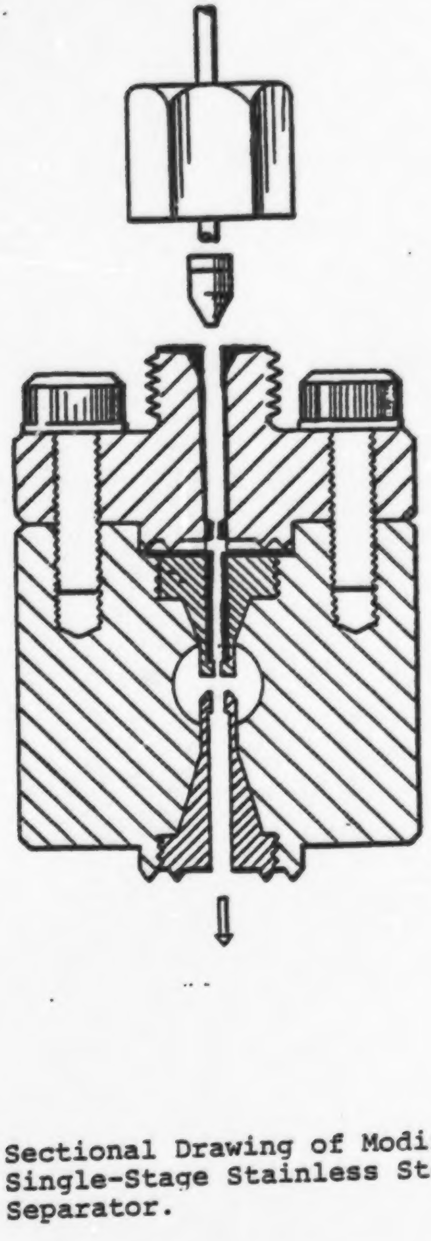


Figure 7.6. Sectional Drawing of Modified Single-Stage Stainless Steel Separator.

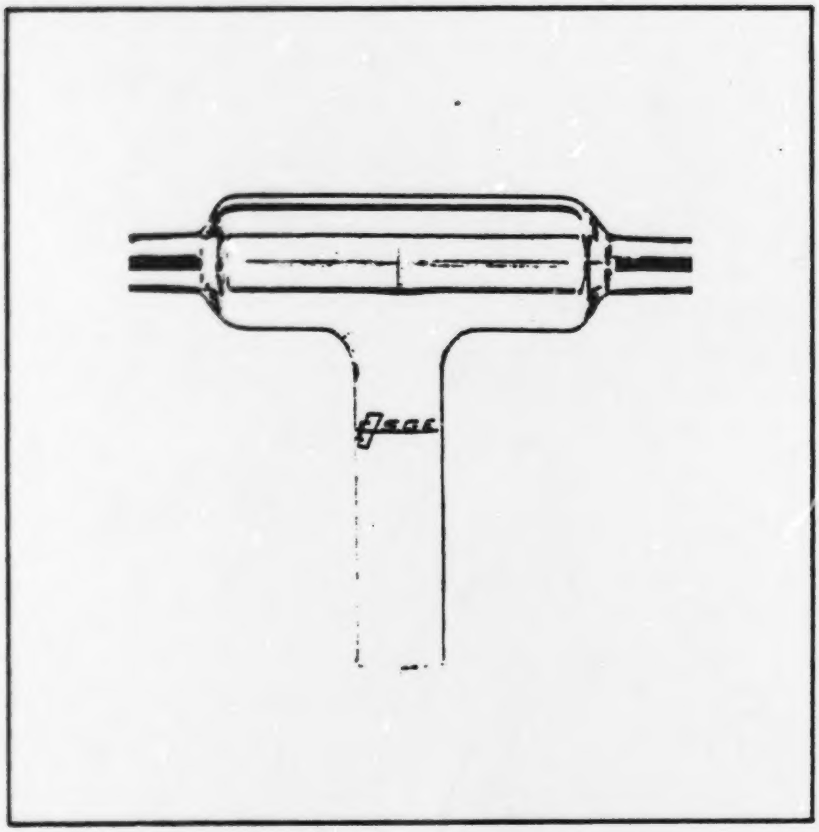


Figure 7.7. Photograph of Single-Stage Glass Jet Separator.

part of the LKB 2091 GC-MS system. A Varian 2400 series gas chromatograph was substituted in its place, although it was necessary to extensively modify this instrument for liquid nitrogen coolant and several other instrumental changes. Specifically, this modified 2400 Varian instrument is now equipped for both split sample injection and on-column injection with fused-silica open tubular columns. To obtain optimum performance at the column exit where the effluent is passed into a hydrogen flame ionization detector, it was necessary to rotate the entire detector assembly on its side so that the fused silica column would terminate properly in the active region of the effluent detector.

Several other modifications have also been incorporated into this reconfigured TDAS. As an illustration, Figure 7.8 is an artist's rendering of the front-end region which shows the glove-box enclosure surrounding the sample entry region. This permits the safe handling of toxic substances and also affords an increased capability in admitting a wider variety of types of samples. For example, the sample insertion region has now been reconfigured so that higher temperatures (up to 700°C) can be applied to the sample insertion chamber. Thus, substances that decompose before they are volatilized can be admitted to the system.

A CDS pyroprobe insert has been incorporated into the sample insertion facility of the TDAS, and this permits polymeric materials to be experimentally investigated along with a variety of other substances which can be placed in special probes such as those shown in Figure 7.9. In addition, the sample insertion region now can accept gaseous samples which can be admitted with a gas-tight syringe. These increased sample handling capabilities, both at the TDAS insertion chamber and at the injection port within the gas chromatograph, permit a wider utilization of the system. With this reconfiguration, standard compounds can be admitted at either location, thus permitting easier quantitations and a more ready access for generating mass spectra for these compounds.

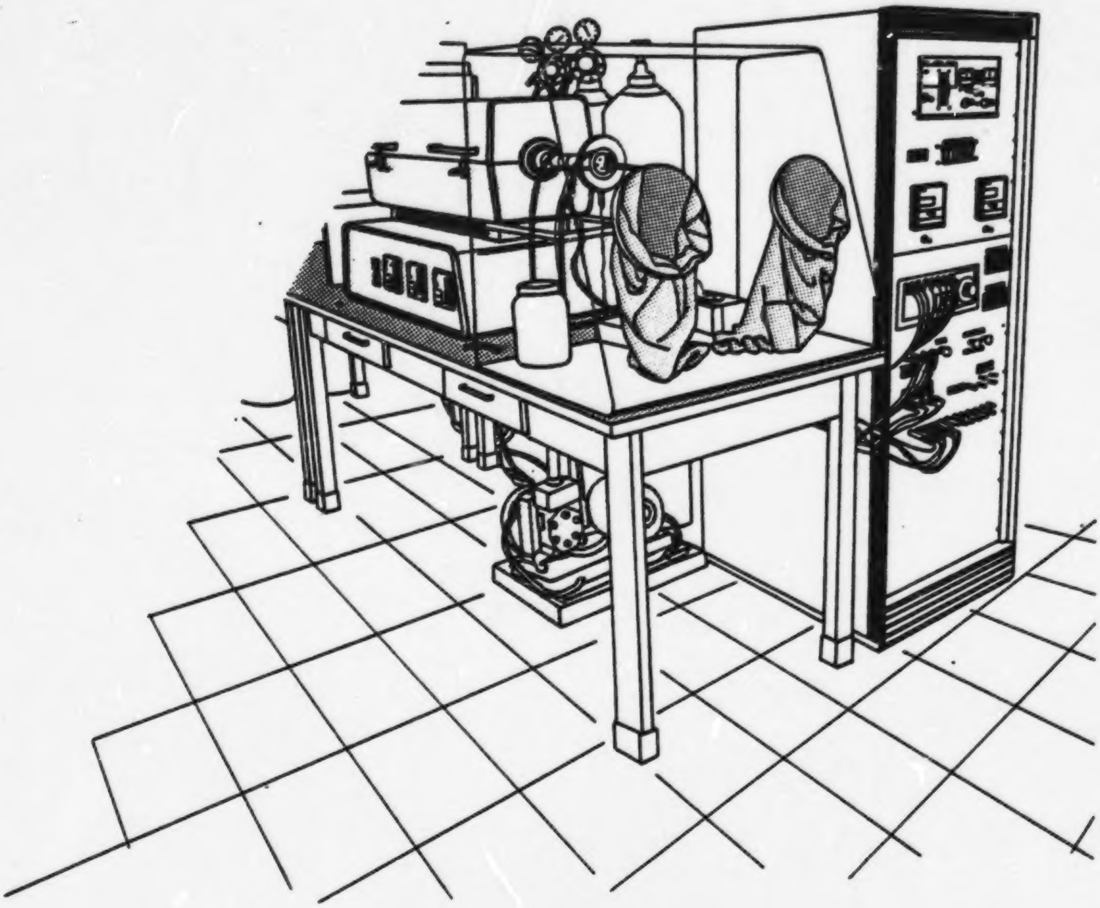


Figure 7.8. Glove-Boxed Front-End of Reconfigured TDAS.

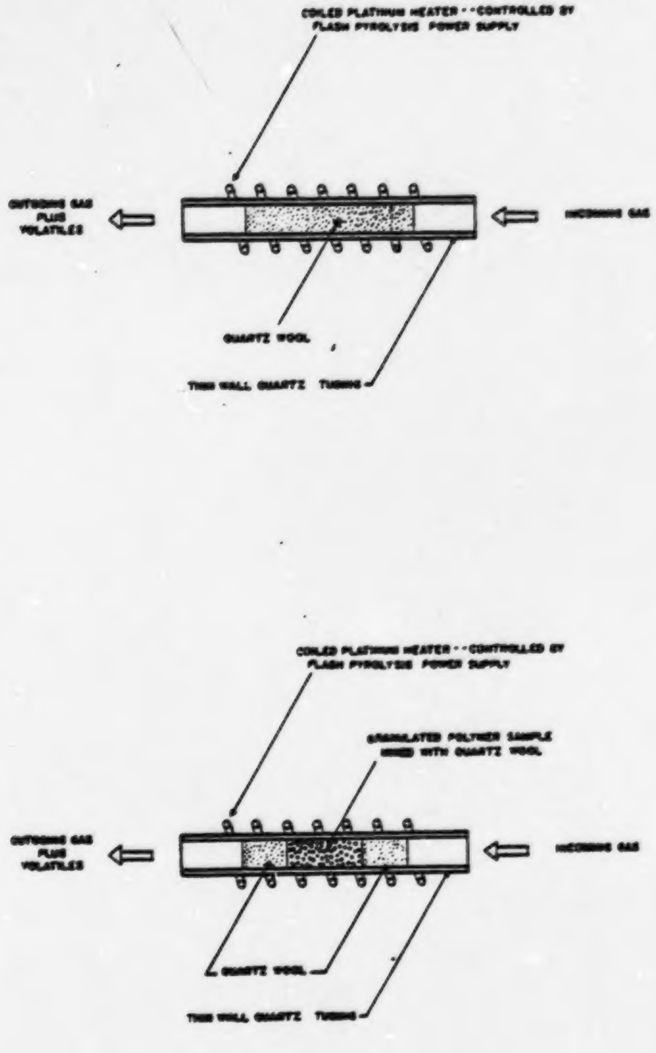

COILED PLATINUM HEATER - - CONTROLLED BY FLASH PYROLYSIS POWER SUPPLY
OUTGOING GAS PLUS VOLATILES
INCOMING GAS
QUARTZ WOOL
THIN WALL QUARTZ TUBING
COILED PLATINUM HEATER - - CONTROLLED BY FLASH PYROLYSIS POWER SUPPLY
GRANULATED POLYMER SAMPLE MIXED WITH QUARTZ WOOL
OUTGOING GAS PLUS VOLATILES
INCOMING GAS
QUARTZ WOOL
THIN WALL QUARTZ TUBING

Figure 7.9. Special Sample Insertion Probes for Reconfigured TDAS.

With the addition of the multiple ion detection package to the mass spectrometer, a new dimension is added to the TDAS. The selective monitoring of several ions characteristic of the compounds that would be of interest during a series of thermal decomposition experiments can now be conducted. The MID also enables a 100 to 1,000 fold increase in detection sensitivity. This is a valuable feature for detecting trace level concentrations that would be generated during thermal decomposition experiments. In addition, the MID capabilities provide a mechanism for independent analysis of compounds that would be chromatographically fused with other solute zones.

SECTION 8

SUMMARY DISCUSSION

Gas-phase thermal destruction of hazardous organic molecules in appropriately designed incinerators is the key to environmentally safe disposal of a significant proportion of the hazardous waste generated annually in the United States. Because of this, the gas-phase thermal decomposition characteristics of a variety of hazardous organic compounds and mixtures of organic compounds has been investigated using the thermal decomposition analytical system (TDAS). Valuable information concerning the thermal stability of mixtures of chlorinated compounds and pure compounds and the formation of products of incomplete combustion (PICs) from parent organic material has been obtained. In addition, the effect of varying the mean residence time and oxygen concentration on the thermal decomposition of chlorinated aromatic compounds has been ascertained.

Comments on certain aspects of the studies described in this report follow. The reader is referred to the complete text for a comprehensive presentation of the experimental results and a thorough discussion of the specific experiments performed.

8.1 THERMAL DECOMPOSITION AND THERMAL REACTIONS OF SELECTED MIXTURES AND COMPOUNDS

Since incinerators are seldom used for the disposal of pure compounds but more likely for the disposal of complex waste mixtures, the gas-phase thermal decomposition of several organic mixtures was included in this study. These mixtures ranged in complexity from an industrial waste to a five component synthetic mixture.

A commercial mixture of polychlorinated naphthalenes was analyzed in dry flowing air at a 2.0 seconds mean residence time. This mixture was adequately destroyed at 800°C and no significant formation of PICs was observed. However, the industrial waste mixture studied under the same experimental conditions was not adequately decomposed at 800°C. The material remaining at that temperature appeared to be largely composed of volatile PICs.

Perhaps the most interesting mixture studied was a synthetic mixture of five components; two halogenated biphenyls, a polynuclear aromatic, a polychlorinated dibenzofuran, and a polychlorinated dibenzo-p-dioxin. This mixture yielded several reaction products at 750°C and these as well as some of the original components of the mixture were detected at 800°C following a 2.0 second exposure in dry flowing air. Subsequent work identified the halogenated biphenyls as the principal precursors to the PICs from the five component mixture and suggested that the products were formed by these two compounds with little effect from the other components in the mixture.

The formation of PICs was also observed in the case of pure compounds. Chloroform, a simple one carbon chlorinated compound was shown to readily form higher molecular weight thermal reaction products, some of which are much more stable than the parent chloroform. It has become well-established that larger chlorinated aromatics may form dibenzo-p-dioxins,[19,20] but little attention has been given to the possibility that even the simplest chlorinated molecules may also lead to the formation of such compounds. Based on data presented within this report as well as reactions described elsewhere,[21] some hypothetical reaction pathways are presented (Figure 8.1).

Pentachloronitrobenzene (PCNB), also studied as a pure compound, demonstrated a very high propensity to form hexachlorobenzene (HCBz). Although PCNB could be destroyed to the 99.99 percent level at 590°C, HCBz required temperatures in excess of 800°C for its destruction. This data illustrates the caution which must be exercised with the use of a single molecular property or parameter as a method of ranking the incinerability of hazardous organic compounds.

To obtain a permit for the operation of a hazardous waste incinerator, the Guidance Manual for Hazardous Waste Incinerator Permits [11] states that the principal organic hazardous constituents (POHCs) of a waste that is intended for incineration must be determined. These POHCs are the hazardous organic

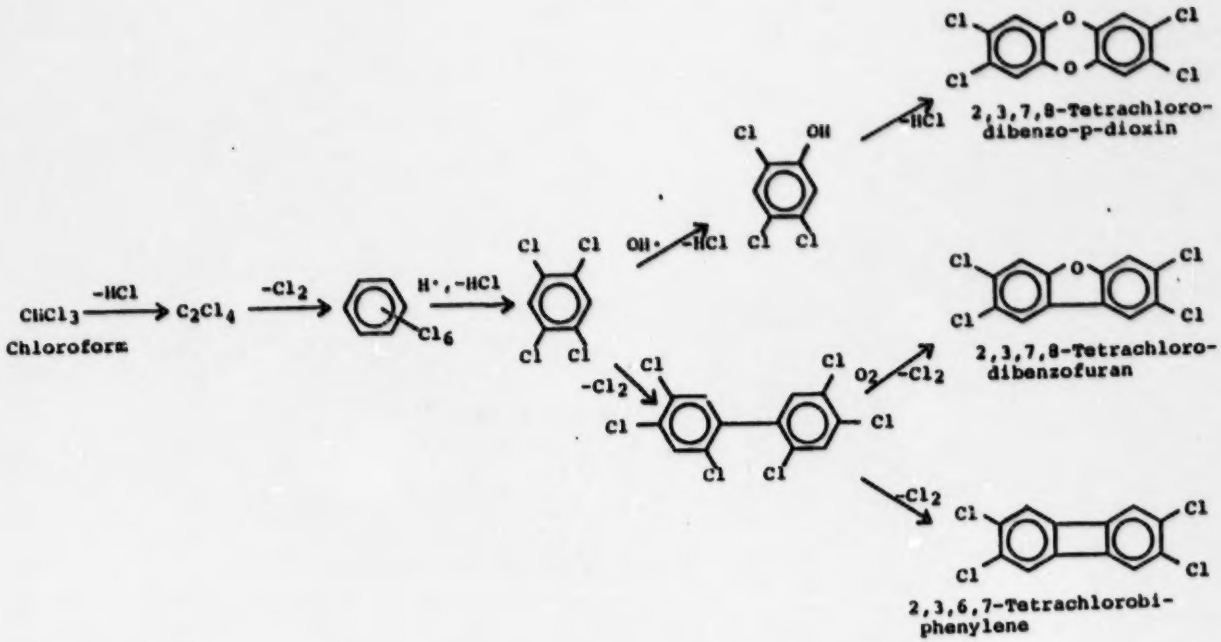

CHCl3
-HCl
Chloroform
C2Cl4
-Cl2
Cl6
H·,-HCl
Cl Cl
Cl Cl
OH·
-HCl
Cl OH
Cl Cl
-HCl
Cl Cl
Cl Cl
O O
2,3,7,8-Tetrachloro-dibenzo-p-dioxin
-Cl2
Cl Cl
Cl Cl
Cl Cl
Cl Cl
O2
-Cl2
Cl Cl
Cl Cl
O
2,3,7,8-Tetrachloro-dibenzofuran
-Cl2
Cl Cl
Cl Cl
2,3,6,7-Tetrachlorobi-phenylene

Figure 8.1. Possible Reaction Pathways for the Formation of Toxic Products of Incomplete Combustion.

constituents of the waste (listed in 40 CFR Part 261, Appendix VIII) that are most abundant and most difficult to burn. The difficulty of burning a compound may be interpreted, as stated in the manual, using the heat of combustion value for the compound. According to the rationale of this method, the lower the heat of combustion of a compound, the more difficult it should be to incinerate. In order for the facility to achieve compliance, a trial burn must demonstrate a 99.99% destruction and removal efficiency (DRE) of the selected POHCs.

Laboratory data generated under this program and presented in this report indicate that appropriate criteria for a POHC selection may be quite complex. If pentachloronitrobenzene (PCNB) was present in sufficient concentration in a waste stream, it could qualify as a POHC. As an Appendix VIII compound with a heat of combustion of 1.62 on a kilocalorie per gram basis, it ranks within the top ten percent of compounds most difficult to burn based on the heat of combustion ranking method. However, based on its low gas-phase thermal stability, this compound may be easily destroyed and may consequently provide a misleading indicator of the incinerator's efficiency. An incinerator operating under conditions based on the 99.99% destruction and removal of PCNB could mistakenly be considered adequate to destroy most of the Appendix VIII compounds. In actuality, based on our laboratory data, these conditions may only destroy the most fragile compounds.

Furthermore, PCNB has been shown to produce HCBz in large quantities. HCBz is one of the most stable compounds we have tested. The optimum conditions required for PCNB destruction appear to coincide with the optimum conditions for HCBz formation. Thus, the incinerator may not only be operating at conditions which would not result in destruction of other POHCs, but could also be maximizing the formation of PICs.

Of the two problems, the failure to address the formation of PICs would appear more serious. Destruction of these products following their formation is complicated by the fact that these products will experience a shorter residence time at high temperature. Because of this, even more severe thermal conditions would be required for destruction of the PICs than would be required for the same constituent in the initial waste feed.

Another method currently available for ranking the incinerability of hazardous compounds is based on $T_{99.99}$, the temperature required for 99.99 percent destruction of the compound (gas-phase, 2.0 seconds residence time in dry flowing air). As in the case of the heat of combustion ranking method, this method fails to address the problem of PIC formation. For example, using this method of ranking, PCNB would rank as very easy to incinerate. Facilities which were permitted based on their ability to successfully destroy compounds with $T_{99.99}$ higher than PCNB would presumably be permitted to burn compounds such as PCNB without conducting trial burns. But, if the facility was permitted based on a compound with a lower $T_{99.99}$ than the PIC HCBz ($T_{99.99}$ >800°C) but higher than PCNB ($T_{99.99} \approx 590°C$) then the operating conditions under which the permit was issued might not be sufficient to prevent emissions of HCBz.

From the above examples, as well as data presented within this report, it should be clear that there is not a single universal parameter adequate for ranking the incinerability of the wide range of organic compounds. However, based on this work, it seems that product formation should play a key role in any incinerability ranking scale and determination of incinerator operating conditions. Instrumentation, like the TDAS, can make a substantial contribution to obtaining the data base required for the development of such a ranking method.

8.2 KINETIC DATA AND OXYGEN EFFECTS FOR SELECTED COMPOUNDS

The gas-phase residence times in the various thermal zones of an incinerator may vary widely depending on the volume throughput and design characteristics of the particular unit. The effect of various residence times at temperature on the thermal decomposition of both a mixture of compounds and a pure compound were studied. In the case of the pure compound, a kinetic treatment of the data enabled calculation of the reaction order with respect to time.

The variation of mean residence time at 750°C for a mixture of five chlorinated aromatic compounds dramatically demonstrated the role of residence time in the efficiency of thermal decomposition. By increasing the time at 750°C from 0.5 to 4.0 seconds, the levels of destruction for all five compounds increased in the range of 64 to 82 percent.

Similar results were obtained for another chlorinated aromatic compound, in this case, a polychlorinated biphenyl. The destruction of this compound at 751°C increased 50 percent with an increase in the mean residence time from 0.5 to 2.0 seconds. Sufficient data were collected for this compound to enable a kinetic treatment of the data. Results of this treatment indicate that this compound is amenable to analysis based on pseudo first-order approximations.

Another variable which was identified as playing a key role in the successful combustion of organic molecules is the oxygen content of the reaction atmosphere. For the case of chlorinated hydrocarbons the stoichiometric requirement for oxygen in combustion processes is expressed by the equations

$$C_xH_yCl_z + (x + \frac{y-z}{4})\ O_2 \rightleftharpoons xCO_2 + 2HCl + \frac{y-z}{2}\ H_2O$$

when $y > z$, or

$$C_xH_yCl_z + xO_2 \rightleftharpoons xCO_2 + y\ HCl + \frac{z-y}{2}\ Cl_2$$

when $y < z$.

Clearly, oxygen must be present in sufficient quantities so that products are those resulting from complete combustion.

Since oxygen concentration in incinerators may vary spatially (e.g., with proximity to air jets) as well as with time (e.g., with changing feed rates or as a result of flare-ups) the impact of varying the oxygen concentration on the thermal decomposition of various compounds is of interest.

In the course of this work, it was demonstrated that polychlorinated naphthalenes and a polychlorinated biphenyl required temperatures exceeding 1,000°C for 99.99 percent destruction in dry flowing nitrogen (2.0 seconds mean residence time). This temperature was 200°C or more higher than the temperature required for the same level of destruction of these compounds in dry flowing air.

A kinetic treatment of polychlorinated biphenyl data as well as data obtained for three chlorobenzenes provided additional insight into the oxygen dependence of the thermal decomposition of chlorinated compounds. It was found that the polychlorinated biphenyl at 700°C along with 1,2,3,4-tetrachlorobenzene and pentachlorobenzene at 725°C all exhibited a first order dependence on oxygen concentration. At higher temperatures, however, the oxygen dependence of the tetrachlorobenzene and the pentachlorobenzene dropped considerably, possibly indicating a shift in thermal decomposition mechanism away from bimolecular processes involving oxygen or oxygen containing species toward unimolecular processes. Hexachlorobenzene, the third chlorobenzene for which an oxygen dependence was determined, had a low reaction order in oxygen throughout the temperature range studied. It is hypothesized that the lack of hydrogen on hexachlorobenzene plays a significant role in its lack of oxygen dependence.

From these data one could surmise that the role of oxygen in incineration is important and quite complex. Thermal destruction zones operating at lower temperatures might, depending on the degree of chlorination of the waste feed, produce significant improvement in destruction efficiency by providing additional air or reducing waste feed rates. Increased air in destruction zones operating at higher temperatures, on the other hand, may result in no improvement in the destruction efficiency of POHCs, but could be expected to decrease PIC emissions.

We have previously discussed incineration failure modes and their drastic impact on overall incineration efficiency.[8] Temperature, residence time, and especially oxygen concentration distribution in the incinerator have been clearly identified as important variables. The important point is that transient operational failures or seemingly small design failures can result in less than optimum control of these variables which can in turn have an enormous (and possibly controlling) effect on the efficiency of the incinerator. The time, temperature, and oxygen dependency data generated and reported here is essential to further understanding and analysis of incineration failure modes.

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APPENDIX

CASE 1

HEX WASTES

Lab Study

Major constituents of hex waste sample were determined to be hexachlorocyclopentadiene (HCCPD), octachlorocyclopentene (OCCP), hexachlorobenzene (HCBz), and pentachlorobenzene (PCBz). HCBz was determined to be a major PIC and was predicted to be the most stable species in the system requiring a temperature greater than 900°C at $\bar{t}_r = 2s$ to achieve 99.99% DE. HCCPD and OCCP were predicted to have a 99.99% DE at temperatures less than 800°C and 600°C respectively at $\bar{t}_r = 2s$.

Reference: "High-Temperature Degradation Characteristics of Hazardous Organic Wastes - A Laboratory Approach", UDRI Draft Report under EPA Grant #R805117-01-0, 1980.

Field Study

Sewage sludge samples from the Morris Forman Wastewater Treatment Plant in Louisville, Kentucky, were determined to contain HCCPD and OCCP as major toxic components along with HCBz and PCBz in somewhat lesser concentrations. Sludge samples were subjected to the pilot scale wet oxidation process at Zimpro Corporation in Rothschild, Wisconsin. The filter cake from the wet oxidation was then incinerated at the Colorado School of Mines in Golden, Colorado (multiple hearth).

OCCP could not be detected in any stack gas samples while HCCPD was detected in trace quantities which corresponds to the predictions of the laboratory study. HCBz and PCBz were the only toxic organics present at measurable levels and HCBz was determined to be the major species in the stack effluent. This is consistent with the lab study on the sludge and subsequent lab studies on pure compounds which have shown PCBz and HCBz to have extreme thermal stability and HCBz to be frequently formed as a product of incomplete combustion.

Reference: "Region IV Support at Morris Forman Wastewater Plant, Louisville, Kentucky," Draft Final Task Report under EPA Contract 68-02-2618, F. C. Whitmore, R. L. Durfee, and M. N. Khattak, Versar, 1977.

CASE 2

p,p'-DDT

Lab Study

Predicted a 99% DE at T= 480°C and a 99.99% DE at $T = 500°C$ for $\bar{t}_r = 1s$. Destruction dependent upon residence time. Predicted formation of o,p'-DDT, p,p'-DDE, and o,p'-DDE as major PICs, each more thermally stable than the parent p,p'-DDT. DDD was observed as a thermally stable impurity in the DDT. The most stable of these was p,p'-DDE with a predicted 99.99% DE of 820°C o,p'-DDE had about the same $T_{99.99}$. Thus the DDE isomers were predicted as limiting the incineration.

Reference: "Laboratory Evaluation of High-Temperature Destruction of Kepone and Related Pesticides", EPA-600/2-76-299, D. S. Duvall and W. A. Rubey, 1976.

Field Study

Test burn conducted on 76.2 cm diameter pilot multiple hearth furnace with afterburner at Envirotech Corporation in Brisbane, California. The major reported PICs were the DDE isomers along with some DDD. The average DRE (which included production of DDE and DDD) at 760°C and 955°C was 99.98% with the production of DDE representing the controlling factor in the complete incineration of DDT. Gas phase afterburner non-flame residence times were not available.

Full-scale test burn was conducted at the Palo Alto Incineration in Palo Alto, California. The incineration was similar to that used for the pilot burn but much larger. DDE was again found to be the major PIC and was the limiting factor in the incineration efficiency. The average DRE (again including PICs) was determined to be 99.97 at an average temperature of 678°C.

Reference: "A Study of Pesticide Disposal in a Sewage Sludge Incinerator", Final Report under EPA Contract 68-01-1587, F. C. Whitmore and R. L. Durfee, Versar, 1974.

CASE 3

PCB

Lab Study

Several PCB isomers were studied, results of which are summarized.

Name	$\bar{t}_r$	T_{99}	$T_{99.99}$
2,5,2',5'-tetrachlorobiphenyl	2.0	745	760
2,5,2',4',5'-pentachlorobiphenyl	2.0	740	760
2,6-dichlorobiphenyl	2.0	800	830
2,2',4,4',5,5'-hexachlorobiphenyl	1.0	720	740
decachloro-biphenyl	1.0	770	820

Numerous PICs were found which included other PCB isomers, chlorinated benzenes, and chlorinated benzofurans. Hexachlorobenzene was a significant product and represented the most stable compound produced by thermal degradation of PCBs, needing about 900°C to be decomposed to 99.99% DE.

References: "Laboratory Evaluation of High-Temperature Destruction of Polychlorinated Biphenyls and Related Compounds", EPA-600/2-77-228, D. S. Duvall and W. A. Rubey, 1977.

"High-Temperature Degradation Characteristics of Hazardous Organic Wastes - A Laboratory Approach", UDRI Draft Report under EPA Grant R805117-01-0, 1980.

Field Study

Full-scale burn conducted at contract disposal facility operated by Rollins Environmental Services, Inc. in Deer Park, Texas. System consisted of rotary kiln and liquid injection burner feeding a common afterburner. The afterburner was operated at a gas temperature of 1300°C with $\bar{t}_r$ = 2-3s and O_2 concentrations of about 10%. DREs of 99.999% were achieved under these conditions which is consistent with laboratory results. Chemical analysis was for the most part conducted by chemical class, thus direct PIC comparison is difficult. Significantly, however, chlorinated benzofurans were detected in the effluent as predicted by the lab studies.

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CASE 4

KEPONE

Lab Study

Predicted a 99% DE at T = 470°C and 99.99% DE at T $\simeq$ 500°C for $\bar{t}_r$ = 1s. Residence time dependent. Hexachlorocyclopentadiene and hexachlorobenzene (HCBz) predicted as PICs with HCBz still present at 900°C which would represent limit on incineration.

Reference: "Laboratory Evaluation of High-Temperature Destruction of Kepone and Related Pesticides", EPA-600/2-76-299, D. S. Duvall and W. A. Rubey, 1976.

Field Study

Pilot scale burn conducted at Midland Ross, Surface Combustion Division in Toledo, Ohio. Consisted of rotary kiln pyrolizer and fume incinerator (afterburner). Results indicated at $\bar{t}_r$ = 2s and T = 1093°C that >99.99% DRE was achieved at all Kepone feed rates. Furthermore, HCBz was detected as the majorPIC and was far more stable than Kepone. Thus, HCBz formation was the limiting factor in Kepone incineration.

Reference: "Kepone Incineration Test Program", EPA-600/2-78-108, B. A. Bell and F. C. Whitmore, 1978.